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VOL. 42 NO. 387 MARCH 1956

THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 26 Portland Place, London, W.1 on 9 November 1955, the Chair being taken by the President, Lt-Col. S. J. M. Auld, O.B.E., M.C., D.Sc.

The General Secretary read the minutes of the meeting held on 12 October 1955. These were confirmed and signed as a correct record. He also announced the names of members elected since the previous meeting.

The Chairman, introducing the authors of the paper to be presented, said: We are here tonight to listen to a paper, entitled "Pre-flame Reactions in Diesel Engines." The authors, Professor F. H. Garner, Dr G. H. Grigg, Professor F. Morton, and Dr W. D. Reid, are from the University of Birmingham.

Professor Garner and Professor Morton have, for some years, been leading a team on this important aspect of ignition and combustion, and it gives me much pleasure to welcome them here tonight with two other members of that team.

The following paper was then presented in summary by Dr G. H. Grigg.

PRE-FLAME REACTIONS IN DIESEL ENGINES* PART III

By F. H. GARNER,† O.B.E. (Past-President), G. H. GRIGG† (Student Member), FRANK MORTON† (Fellow), and W. D. REID† (Student Member)

SUMMARY

The occurrence of pre-flames in a diesel engine has been investigated using a photomultiplier unit, and the chemical reactions during the pre-flame period have been followed by sampling the combustion chamber gases, withdrawn from the chamber by means of an electromagnetically operated mushroom-type sampling valve. The design and testing of the valve is described. Two types of pre-flame have been observed; a high intensity pre-flame occurring before injection of the fuel, and a secondary pre-flame of low intensity. These pre-flames are accompanied by high concentrations of aldehydes, and are dependent upon fuel composition, injection timing, and engine conditions.

With a high cetane number paraffinic fuel, pre-flames of low intensity occur at or after the point of injection for both early and late injection timings. On the other hand, with a low cetane number naphthenic fuel pre-flames of high intensity occur before injection, with late injection timings. These high intensity pre-flames are believed to be due to unburnt fuel from the previous cycle, and may be characteristic of low cetane number fuels.

The mechanism of oxidation in a diesel engine is discussed.

INTRODUCTION

A FULL understanding of the combustion reactions of hydrocarbons in a compression ignition engine is of importance in the development of suitable fuels and additives for use in the modern light-weight, high-speed diesel engine. The chemical reactions preceding the flame are complex, and efforts have been made to study the pre-flame reactions by analysing samples of the combustion chamber gases at various positions in the stroke.

In an earlier publication,[1] a sampling valve was described, designed primarily for a Crossley single cylinder type BVC-1 diesel engine. The valve, with an opening time of 2° crank angle at the engine operating speed (1200 rev/min), was operated by an hydraulic mechanism using oil at high pressure and controlled by a valve timing gear to give the required opening time. With the valve opening 2° crank angle, a gas flow from the swirl chamber of 30 ml/min was obtained. Using this valve, samples of combustion gas from the chamber were collected, and subsequently analysed, to determine the amount of aldehydes and peroxides present in the combustion chamber gases at various positions of the stroke from −10° to +4° crank angle. Four fuels were used at injection timing −8° and full load, and one of the fuels was examined at half load.

The results of this preliminary work showed that peroxides and aldehydes were formed by the reaction of the injected fuel with the hot compressed air, but that when misfiring occurred with a low cetane number fuel, peroxides and aldehydes were present in the combustion chamber prior to fuel ignition, owing presumably to pre-flame reactions occurring during the compression stroke, and involving unburnt fuel from the previous cycle.

The presence of chemical intermediates in the combustion chamber during the pre-flame period suggested that pre-flames might occur in the diesel engine as with the spark-ignition engine. It was decided to investigate the presence of pre-flames with a photomultiplier unit similar to that described by Downs, Street, and Wheeler,[2] and to investigate the occurrence of chemical intermediates in samples taken during that period of the stroke over which pre-flames had been shown to occur. This required sampling over a much wider range on the compression stroke than had been

* MS received 16 August 1955.

† University of Birmingham, Chemical Engineering Department.

attempted previously, and involved a study of the effect of variation of injection timing, engine load, fuel rate, and fuel characteristics.

The hydraulically operated valve was unsuitable for this programme because of the low rate of gas flow (30 ml/min). A magnetically operated valve was constructed which gave a higher rate of gas flow (400 ml/min) for the same opening time, namely, 2° crank angle. This valve has been used to obtain samples of combustion gases from the Crossley engine over a wide range of crank angle positions, for various fuel injection timings and for two different fuels. The analysis of these samples is discussed in relation to the appearance of pre-flames in the engine.

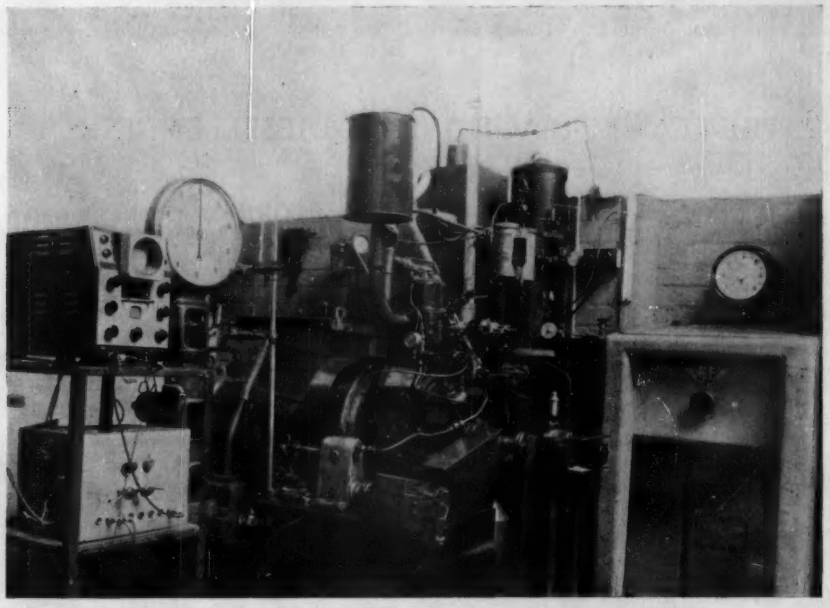


FIG 1

GENERAL LAY-OUT OF ENGINE AND EQUIPMENT

EQUIPMENT

The general lay-out of the apparatus is shown in Fig 1. The engine used throughout this work was a single cylinder Crossley–Ricardo diesel engine fitted with a Mark II "Comet" type cylinder head containing a spherical combustion chamber (Fig 2). Details of the engine performance and operating conditions are given in Table I.

The engine was coupled to a Heenan and Froude dynamatic dynamometer, by which the engine speed could be kept constant and independent of the load. The surge chamber on the air intake contained a heater, and constant jacket temperature was maintained by an immersion heater and thermostat fitted in the cooling water system.

The equipment was modified so that the injection timing could be varied whilst the engine was running. The Crossley injection pump was replaced by a CAV pump, which was driven at half engine speed from the crankshaft through a 1 : 2 ratio chain drive and a set of phasing gears, as shown in Fig 3. Using these phasing gears, the injection timing could be set at any desired position. "Whip" in the driving chain was reduced to a minimum by means of a heavily spring loaded jockey sprocket wheel.

The engine could be operated under eight stroke conditions by injecting fuel every four crankshaft revolutions. This was achieved by fitting a by-pass valve in the fuel line between the injection pump and the injector, as shown in Fig 3. This valve, operated by a cam driven by bevel gears from the pump shaft, opened every two revolutions of the injection pump and allowed the fuel to flow away to a vane type pump, from which it was returned to the fuel tank. On the other revolutions of the injection pump, the valve was

TABLE I

Speed	1200 rev/min
Maximum rated output	7 b.h.p.
Stroke	4·5 inches
Bore	4·0 inches
Compression ratio	17·55
Injection nozzle	CAV pintle type
Injector opening pressure	1800 p.s.i.
Inlet valve opens	−13° crank angle
Inlet valve closes	+190° crank angle
Exhaust valve opens	+167° crank angle
Exhaust valve closes	−8° crank angle
Lubricating oil	SAE 40
Fuel consumption *	26 ml/min
Outlet water temperature	175° F
Inlet air temperature	105° F

* Unless otherwise stated.

closed and the fuel flowed to the injector. Injection every four revolutions could have been obtained by running the pump at quarter crankshaft speed, but

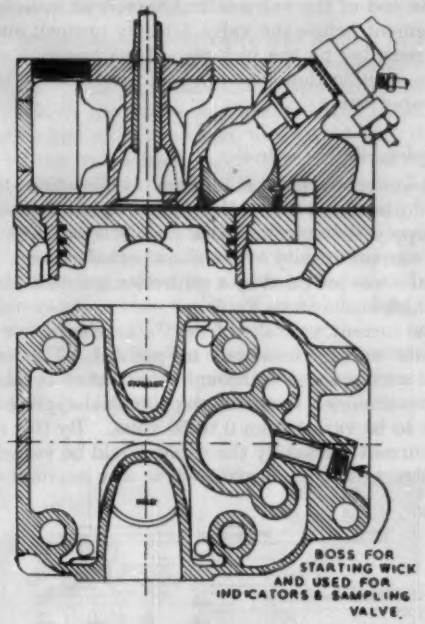


FIG 2

CROSSLEY CYLINDER HEAD

this would have altered the pump characteristics and doubled the period of injection. With the by-pass valve, the injection characteristics were the same for eight-stroke and four-stroke operation, because the pump speed remained the same.

Engine Indicators

Standard Sunbury indicating equipment was fitted to the engine for the measurement of the crank angle positions of injection and ignition. These indicators were connected to a Cossor double-beam oscilloscope. A time sweep and degree marker unit was coupled to the engine crankshaft, and this triggered the time base of the oscilloscope and supplied the signal for the

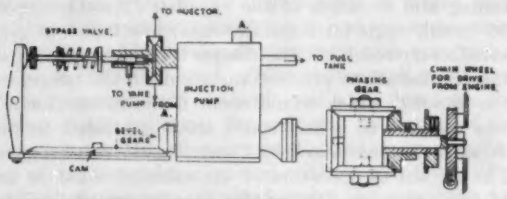


FIG 3

ARRANGEMENT OF INJECTION PUMP, PHASING GEARS, AND BY-PASS VALVE

horizontal degree scale on one of the two beams. An electromagnetic pick-up attached to the injector was used to determine the point of injection.

Fuels

Two fuels of differing character were used throughout the work: D1, the high-cetane number secondary reference fuel, cetane number 70, paraffinic in character, and D6, a naphthenic gas-oil, cetane number 32. Full details of these fuels are given in Table VII of the previous publication.[1]

The Electromagnetic Sampling Valve

The hydraulically operated valve was not suitable for an extensive programme of testing, since the quantity of gas delivered (30 ml/min) was too small to allow a complete sampling run, from −30° to +4° crank angle, to be completed in a reasonable time. Attempts to increase the rate of gas flow resulted in an increase in the opening time above 2° crank angle, with consequent reduction in the accuracy with which the relationship between the appearance of pre-flame intermediates and crank angle position could be compared. This limited opening of the valve was believed to be due to mechanical compression of the valve stem spindle requiring the building up of the force necessary to open the valve against the gas pressure in the combustion chamber.

The electromagnetically operated needle type valve described by Wheeler, Downs, and Walsh [4] had an opening time of 3° crank angle, but did not give a sufficiently high gas flow rate for our investigations. It was felt that the electromagnetic pulse "hammer" principle applied to the mushroom type valve would be satisfactory and would enable high rates of gas flow to be obtained.

To achieve a high rate of gas flow and minimum opening times with a mushroom type valve, the valve head should open immediately to its maximum

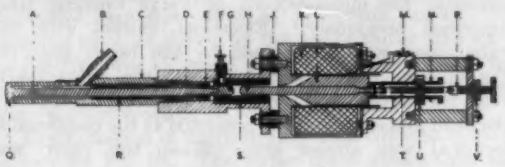


FIG 4

ELECTROMAGNETIC GAS SAMPLING VALVE

position, remaining fully open for the required period of time and subsequently close almost instantaneously. This effect can be achieved by forcing the valve stem to move against the action of a heavy spring by means of a hammer-like pulse, the pulse being produced by an electromagnet. Details of the valve are shown in Fig 4.

The valve stem and body were made of 3 per cent nickel steel, with the valve head and seat, Q, stellite faced. The valve stem was supported in a tufnol guide, R, and was spring loaded by a strong compression spring, D, held in position by the tufnol collar, E. This was locked in position by a mild steel anvil, G, screwed to the end of the valve stem.

The operation of the valve was as follows: The hammer, consisting of a mild steel core, L, and a brass

striking pin, H, was accelerated by a transient magnetic field produced by the solenoid, K. The hammer moved in an axial direction, struck the anvil, and was then returned to its original position by the spring, T. The tension in T could be adjusted by the screw, P, and the movement of the core was limited by the adjustable stop, N. The close fit of the anvil and the hammer in the guide, S, ensured that the valve stem moved only in an axial direction during operation.

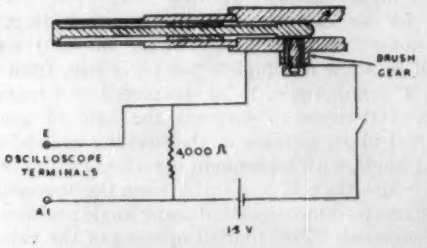


FIG 5
SAMPLING VALVE INDICATOR

When the valve opened, the sampled gases passed down the annulus between the valve body and stem, and out through the tube, B. To reduce the time of flow through the valve, an asbestos bush was fitted to the inside of the valve body, reducing the annulus width to $\frac{1}{64}$ inch, and thus increasing the gas velocity.

Tufnol components were used to insulate the valve stem from the body at all points except between the valve head and seat, which formed a make and break switch for the indicating mechanism.

Valve Indicating Mechanism

Fig 5 shows a modification of the make and break indicator for measurement of valve opening time described previously.[1] Electrical contact with the valve stem was maintained by the brush gear (F, Fig 4), which was insulated from the valve body. With the valve closed the circuit was completed across the head and seat, and the potential at the oscilloscope terminal was almost zero. When the valve was

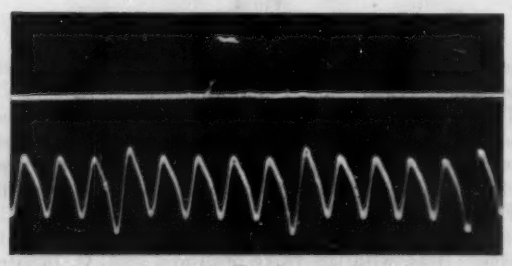


FIG 6
INDICATION WAVE FOR SAMPLING

opened the contact across the head and seat was broken, and since the valve stem was completely insulated from the body by the tufnol components, the electrical circuit was opened. This produced a square wave on the oscilloscope screen (Fig 6).

The advantage of this type of indicator was that it gave a direct indication of valve opening. With an indicator using an electromagnetic pick-up placed near to the end of the valve stem,[1] there was considerable movement before the valve actually opened, and this was recorded by the pick-up. Thus measurement of valve opening time and position were subject to considerable errors.

Sampling Valve Controller

In order to give maximum acceleration to the moving iron core of the electromagnet, it was necessary to supply the solenoid with an electrical impulse of high current density over a short period of time. This impulse was provided by a controller, a circuit diagram of which is shown in Fig 7.

The current was taken from the anodes of five beam tetrode valves connected in parallel. The control grids were connected through two contact breakers to a potentiometer, to enable the potential applied to the grids to be varied from 0 to 50 volts. By this means the current carried by the valves could be varied, and the strength of the impulse set to any required value.

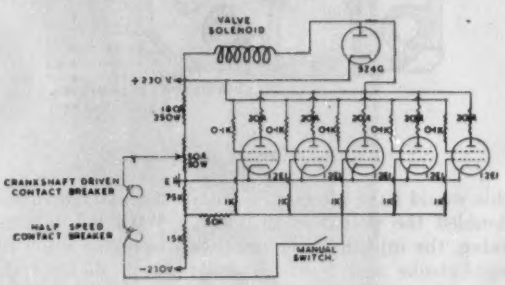


FIG 7
CIRCUIT DIAGRAM OF SAMPLING VALVE CONTROLLER

The valves were " fired " by completing the control grid circuit by means of the two contact breakers. The half-speed contact breaker closed during the compression and power strokes and opened during the exhaust and intake strokes. The other contact breaker, which was coupled directly to the crankshaft, was wired in series with the first, and controlled the timing and duration of the impulse. An impulse of 36° crank angle (or 5 milliseconds) was found to give satisfactory results. The master breaker was fitted to the crankshaft to prevent variations in the timing of the impulse, which would occur if the master switch was coupled to a half speed shaft subjected to the usual variations caused by " lash " in the driving gear. The instant of operation of the solenoid could be set at any point by altering the angular position of the contacts on the master breaker.

When the master contact breaker opened, the current supplied to the sampling valve was stopped abruptly by a negative potential of −75 V applied through a high resistance to the control grids. To protect the beam tetrodes against the back e.m.f.

produced by induction effects, a diode was connected across the terminals of the solenoid.

Operation of the Sampling Valve

The performance of the valve was studied in a test rig (Fig 8), before using it for sampling experiments in the engine. The rig consisted of a steel tube into one end of which the valve was inserted, the other end being blanked off. A pick-up was placed with its tip close to the valve head, and was supported by an adaptor soldered to the end of the valve body. In this way the movement of the valve head in relation to the valve seat could be detected by the pick-up, and any compression effects in the valve body were avoided. The rig was connected to an air cylinder and to a pressure gauge so that the valve could be subjected to a known pressure.

The sampling valve was connected to the controller, and the circuit breakers were driven by the engine running at its normal speed.

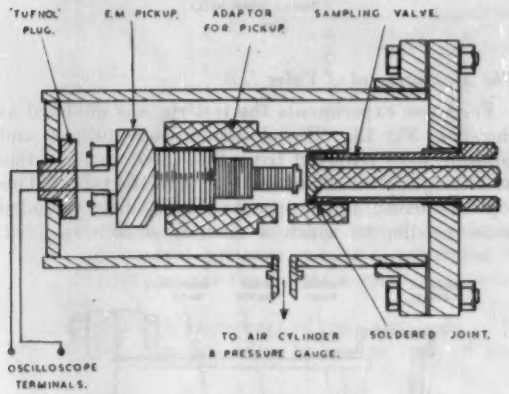
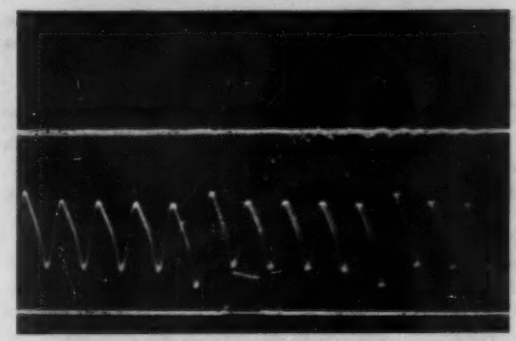


Fig 8

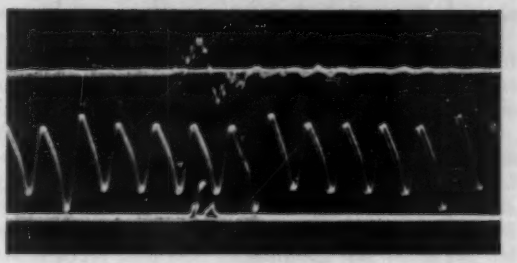
PRESSURE RIG FOR TESTING SAMPLING VALVE

Indicator Diagrams

Fig 9 (*a*) shows the type of diagrams given by the two indicators. The lower trace shows the square wave form of the valve make and break indicator, the middle trace is the degree scale in which each division represents 2° crank angle, and the upper trace was produced by the electromagnetic pick-up situated close to the valve head. This photograph was taken for a rig pressure of 450 p.s.i., and a gas flow from the valve of 450 c.c/min. By reducing the travel of the iron core in the electromagnet, a stage was reached at which the valve operated without gas flow. The indicator diagrams obtained under this condition are shown in Fig 9 (*b*). It appears that without gas flow there was considerable movement of the valve head, lasting for about 4° crank angle, as recorded by the pick-up. Under the same conditions, the sampling valve indicator gave a triangular wave, owing to variation of the electrical resistance between the valve



(*a*) GAS FLOW—450 C.C/MIN



(*b*) NO GAS FLOW

Fig 9

head and seat. The pointed top of the wave suggests that the circuit was broken completely.

When operating normally, as in Fig 9 (*a*), the movement of the valve head, as shown by the pick-up, occurred for about 5½° crank angle. Therefore, the opening time during which gas flow occurred was given by the difference between the readings for normal flow and zero flow, that is, 1½° crank angle. The opening time, as shown by the top of the square wave in Fig 9 (*a*), was 1½° crank angle. This proved that the make and break indicator fitted to the sampling valve gave a true record of its opening period.

The variation in valve timing from cycle to cycle is shown by Fig 10. The upper trace shows that the valve movement was identical for two consecutive

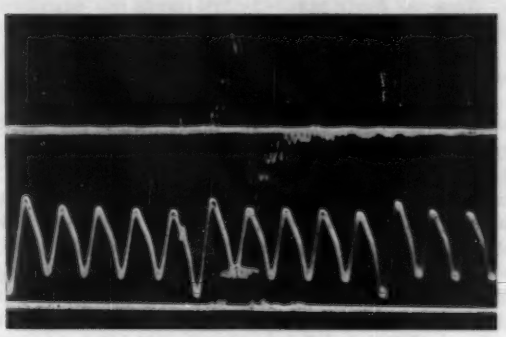


Fig 10

VALVE INDICATOR SHOWING CYCLIC VARIATION OF VALVE TIMING

cycles, whilst the lower trace indicates that the variation in opening time for three consecutive cycles was about $\pm\frac{1}{4}°$ crank angle.

The Effect of Pressure and Opening Period on Gas Flow

Experiments were carried out using the test rig, in which the pressure was varied from 250 to 650 p.s.i., and the gas flow measured for a constant valve opening

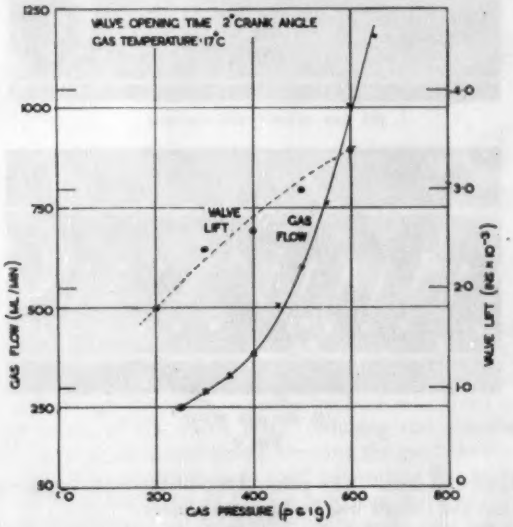


Fig 11

time of 2° crank angle. The results are presented in Table II.

Table II

Effect of Pressure and Opening Time on Gas Flow

Valve opening time 2° crank angle		Pressure 400 p.s.i.	
Pressure, p.s.i.	Gas flow, c.c/min	Opening time, deg crank angle	Gas flow, c.c/min
250	253	$\frac{1}{4}$	89
300	293	$\frac{1}{2}$	167
350	333	2	387
400	387	3	625
450	507	4	1010
500	603	5	2360
550	767		
600	1012		
650	1185		

From the full curve in Fig 11, it is seen that the flow increases rapidly with increase in pressure above 450 p.s.i. During the sampling work described later, a valve opening time of 2° crank angle was used in all the experiments.

Flow measurements were made at a constant pressure of 400 p.s.i. for opening times of from $\frac{1}{4}°$ to 5° crank angle. The results are given in Table II, and plotted in Fig 12 (full curve).

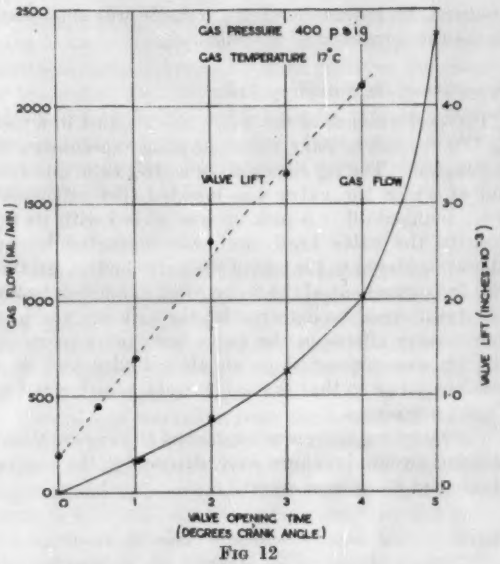


Fig 12

The Measurement of Valve Lift

For these experiments the test rig was modified as shown in Fig 13. The electromagnetic pick-up and adaptor were removed from the valve and a tufnol insulating top was fitted at the end of the tube. This top was drilled and tapped to take a finely threaded brass needle, to which a circular scale was fixed.

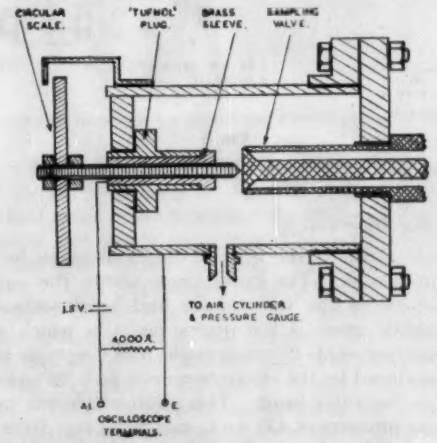


Fig 13

RIG FOR MEASURING VALVE LIFT

The needle and steel tube were connected to the oscilloscope, with a high resistance across the terminals and a battery in the circuit.

The rig was pressurized and the needle was screwed in until contact was made with the valve head, thus completing the electrical circuit and causing a " kick " on the oscilloscope screen. The angular reading on

the circular scale was taken, the needle screwed out, and the sampling valve was then operated without gas flow. The needle was screwed in until it touched the valve head as indicated by the " kick " on the screen, and a second measurement on the scale was made. Knowing the pitch of the thread on the needle, and from the angular difference between the first and second readings, the valve lift for " zero " opening time was calculated and found to be 0·0004 inch.[1, p. 317]

Using this method, the extent of valve lift was determined for opening periods of from $\frac{1}{2}°$ to 4° crank angle at constant pressure, and for pressures from 200 to 600 p.s.i. at a constant opening time of 2° crank angle. The results are given in Table III.

TABLE III

Effect of Pressure and Opening Time on Valve Lift

Opening time 2° crank angle		Pressure 400 p.s.i.	
Pressure, p.s.i.	Valve lift, inches × 10^{-3}	Opening time, deg crank angle	Valve lift, inches × 10^{-3}
200	1·8	0	0·4
300	2·4	$\frac{1}{2}$	0·9
400	2·6	1	1·4
500	3·0	2	2·6
600	3·4	3	3·3
		4	4·2

These results are plotted as the dotted curves in Figs 11 and 12. It appears that the relationship between valve lift and opening period is almost linear, for constant pressure, whilst the increase in valve lift with pressure rise becomes smaller at higher pressures.

The 0·0004-inch movement of the valve head without gas flow may be owing to one or both of two factors :

(1) Since the valve body is in compression owing to the valve return spring and pressure on the valve head, the valve head and seat will move together for a short period before the valve opens and gas flow begins.

(2) The centre of the valve head from which measurements were taken may move before the edges of the valve, owing to a flexing of the head.

Adjustments on the Sampling Valve

The experiments with the test rig showed that the valve could be adequately controlled by the following adjustments :

(1) The adjustment of the stop limiting the travel of the iron core was found to have a marked effect on both the gas flow and the opening period. Increase in core travel was accompanied by increase in both the flow and opening time. Also, the valve timing was slightly retarded. The optimum value for travel of the core was found to be about $\frac{3}{16}$ inch.

(2) The magnitude of the electrical pulse could be varied by the potentiometer, which was found to give finer control of gas flow and opening time without affecting the instant of valve opening.

(3) The tension in the core return spring was found to have a marked effect on the cyclic variation of valve timing, increase in tension tending to reduce the variation.

SAMPLING EXPERIMENTS

The early experiments with the electromagnetic sampling valve were carried out using the high cetane secondary reference fuel, D1, to determine the effect of certain variables on the sampling results. A fixed injection timing of −9° c.a. was used, the sampling range covered being from −12° c.a. to +8° c.a., enabling a complete set of aldehyde and peroxide curves to be obtained in a single run.

The first series of experiments were carried out under standard conditions, with the engine running at half load (b.m.e.p. = 44 p.s.i.). Samples were taken from the combustion chamber at intervals of 2° c.a., with the mushroom valve placed so that its tip was flush with the wall of the chamber. In these and subsequent experiments, fine particles of carbon always appeared in the samples at about +4° c.a., and the amount increased as sampling was taken beyond this point. After sampling beyond +4°, samples were taken before +4° and no carbon was detected, thus showing that the carbon was not being produced from the valve stem as a result of prolonged running. Runs were also made at an increased load (b.m.e.p. 77 p.s.i.).

The results[3] showed that peroxides and aldehydes were present in the combustion chamber during the pre-flame period, and that the concentrations of these intermediates varied during this time. Although the absolute concentrations were not entirely reproducible, the general shape of the curves was the same. Increase in the engine load had little effect on the peroxide curve, the concentration of peroxides and the position of the main peak being unaltered. The concentrations of aldehydes, however, were approximately half those obtained under light load, and the main aldehyde peak occurred earlier. This may be owing to the lower temperatures which occur in the engine under light load conditions, and which favour the formation and stability of aldehydes.

To determine the effect of position of the sampling valve, the mushroom valve was screwed into the combustion chamber a further $\frac{1}{4}$ inch, a distance corresponding to one-third of the radius of the chamber. The concentrations of intermediates (for a b.m.e.p. 44 p.s.i.), were of the same order as those found when the valve was flush with the wall of the chamber. This suggests that at any given time in the pre-flame period, the concentration of intermediates near the centre of the chamber are similar to those at the wall. Owing to the difficulty of finding a suitable place in the cylinder head to bore a second hole into the chamber, no further experiments on the effect of valve position could be carried out.

When sampling with the mushroom valve, the valve head probably caused a certain amount of disturbance to the swirl of gas in the combustion chamber. To find whether this disturbance was appreciable, runs were carried out with a needle type of valve (identical to that employed by other workers [4]), placed flush with the chamber wall. Such a valve should cause no interference with swirl. It was found that the concentrations of peroxides and aldehydes were similar to those obtained with a mushroom valve under the same conditions. The opening time of the needle valve was longer, and thus smoother curves were obtained. Particles of carbon also appeared at +4° crank angle, as was found with the mushroom valve.

MEASUREMENT OF FLAME INTENSITY AND POSITION

In the investigation of cool flame formation in a motored engine,[2] Downs, Street, and Wheeler used a photomultiplier unit, RCA 931, to detect cool flames. This cell has a high internal amplification of approximately 10^6, and a peak spectral response of 4200° Å (approximately the blue-violet region). It was therefore decided to use such a unit in the detection of pre-flames in the diesel engine. As the pre-flame is followed by a hot flame, the phototube was preserved from overload and damage by a series of ten 100-K resistors, that is, one 100-K resistor for every stage of the photomultiplier.

The cylinder head of the Crossley engine is shown in Fig 2. The boss for indicators and the sampling valve were used to take the adaptor (Fig 14). As shown, this

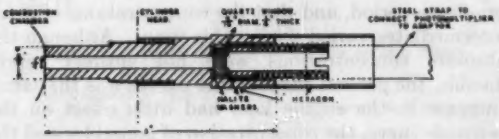


FIG 14

ADAPTOR FOR FLAME MEASUREMENTS

adaptor contained a quartz window, sealed into the adaptor by means of Halite washers. A steel strap connected the photomultiplier tube to the adaptor, the whole unit being light-proof, except for the light which was transmitted from the combustion chamber.

To the first stage of the phototube, 1200-V stabilized d.c. voltage passed from a power pack, and the output from the last stage was passed through a 750-Ω resistor to earth. The voltage drop across the resistor was lead to a Cossor double beam oscilloscope, giving the flame intensity trace. The other beam was supplied from a triggered time base, giving a horizontal degree scale. In the event of carbon formation on the window, further amplification of the intensity could be obtained from the oscilloscope itself.

Runs were carried out at various injection timings and fuel rates. These results are shown in Tables IV–VIII, and plotted in Fig 15, as ignition delay *v.* injection timing. For any one fuel input rate, records were made of the appearance of the main flame, and any pre-flames which occurred, at all injection timings

TABLE IV

*Fuel D*1. *Fuel Rate* 20 *ml/min Degrees Crank Angle*

Injection	Position of pre-flame peak	Appearance of main flame	Delay between injection and main flame	B.m.e.p., p.s.i.
+10	no pre-flame	+20	10	13
+ 5	+10	+16	11	18
0	no pre-flame	+ 9	9	24
− 5	,,	+ 4	9	26
−10	,,	− 1	9	26
−15	,,	− 6½	8½	22
−20	,,	−10	10	20
−25	,,	−14	11	9
−30	,,	−18	12	9
−35	,,	−21	14	6·5
−40	,,	−28	12	4
−45	−41	−33	12	4
−50	no pre-flame	−46	4	—

TABLE V

*Fuel D*1. *Fuel Rate* 26 *ml/min Degrees Crank Angle*

Injection	Position of pre-flame peak	Appearance of main flame	Delay between injection and main flame	B.m.e.p., p.s.i.
+10	+10	+20	10	20
+ 5	− 3	+18	13	31
0	trace	+ 9½	9½	40
− 5	no pre-flame	+ 4	9	44
− 7	,,	+ 2½	9½	44
−10	,,	0	10	42
−15	,,	− 5	10	42
−20	,,	−10	10	35
−25	,,	−13	12	29
−30	−30 to −18	−18	12	24
−35	−30	−17	18	13
−40	−41	−20	20	13
−45	no pre-flame	−41 and −28	4 and 17	11
−50	,,	−41 and −24	9 and 26	9
−55	,,	−38	17	7
−60	,,	−40	20	4

TABLE VI

*Fuel D*1. *Fuel Rate* 32 *ml/min Degrees Crank Angle*

Injection	Position of pre-flame peak	Appearance of main flame	Delay between injection and main flame	B.m.e.p., p.s.i.
+ 5	−5	+18	13	44
0	+4	+10	10	49
− 5	trace at 0	+ 3	8	57
−10	trace	− 1	9	62
−15	no pre-flame	− 6	9	57
−20	,,	− 9½	10½	49
−25	,,	−14½	10½	44
−30	,,	−17	13	35
−35	−34	−20	15	26
−40	−40	−27	13	26
−45	−36	−30	15	26
−50	−36	−31	19	22

for which the engine would operate at the normal speed of 1200 rev/min. This entailed a wide range of injection timings, both before and after the normal injection timing of approx 9° before t.d.c.

Photographic records were also made for certain injection timings at a fixed fuel input of 26 ml/min. These are shown in Figs 16–27. In these figures the upper trace is the horizontal degree scale, in which the highest vertical stroke marks the position of t.d.c., approached from left to right on the compression stroke. The lower trace is the flame intensity curve in which the lowest point is the point of maximum intensity. (This is owing to the supply of a negative voltage to the photomultiplier.)

TABLE VII

Fuel D1. Fuel Rate 80 ml/min Degrees Crank Angle

Injection	Position of pre-flame peak	Appearance of main flame	Delay between injection and main flame	B.m.e.p., p.s.i.
0	no pre-flame	+11	11	66
− 5	—	+ 6	11	73
−10	—	+ 2	12	75
−15	—	− 5	10	75
−20	—	− 9	11	66
−25	−34	−13	12	57
−30	−33	−14	16	44
−35	−32	−18	17	53
−40	−37	−20	20	49

TABLE VIII

Fuel D6. Fuel Rate 26 ml/min Degrees Crank Angle

Injection	Position of pre-flame peak	Appearance of main flame	Delay between injection and main flame	B.m.e.p., p.s.i.
+10	0 and −22	+23	13	14
+ 5	−20 and −12	+22	17	24
0	−19 and −4	+20	20	35
− 5	−20 to +8	+10	15	35
−10	−30, −18, and 0°	+ 6	16	35
−15	no pre-flame	− 2	13	31
−20	,,	− 5	15	—

To clarify the interpretation of the flame intensity photographs, consider Figs 16 and 18. In both diagrams, reading from left to right, the crank angle (c.a.) positions are marked for every 10°. Fig 16 shows the occurrence of a low intensity pre-flame (−21° to +10°), followed by the main flame (between +16°

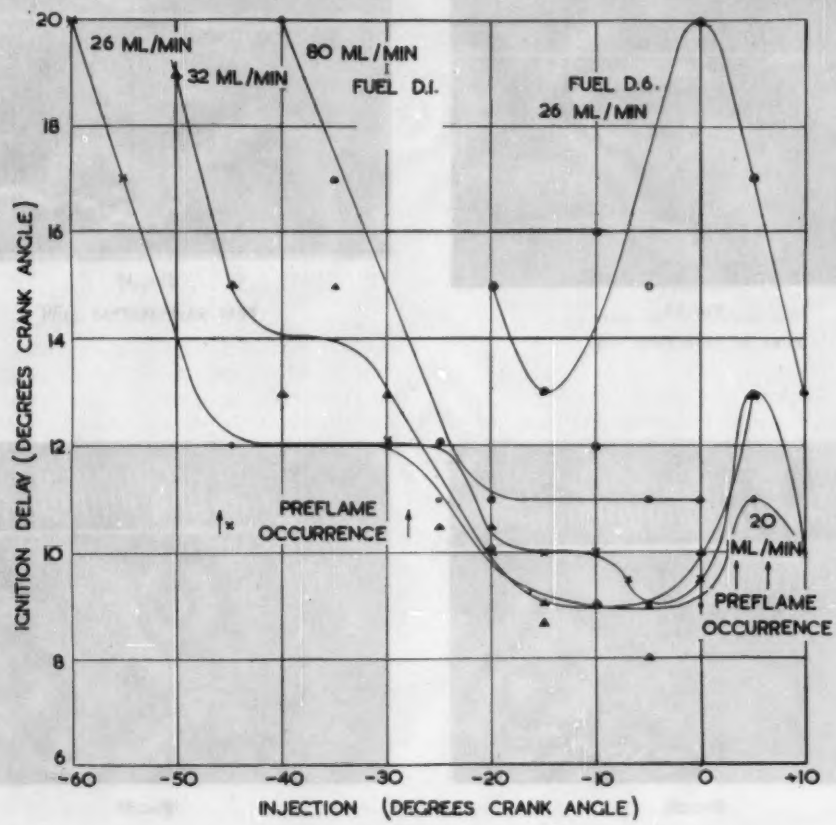


FIG 15

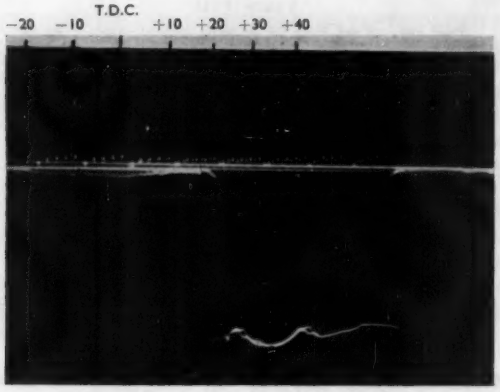


FIG 16
FUEL D1 INJECTION +5°

FIG 17
FUEL D1 INJECTION −0°

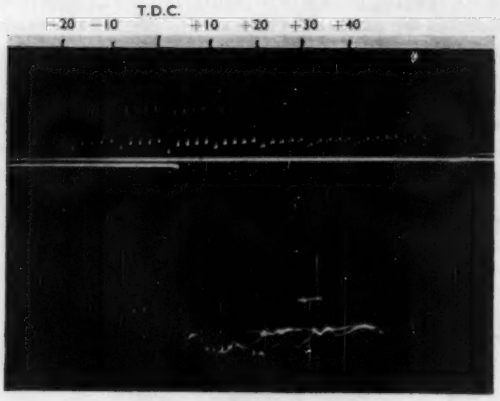


FIG 18
FUEL D1 INJECTION −5°

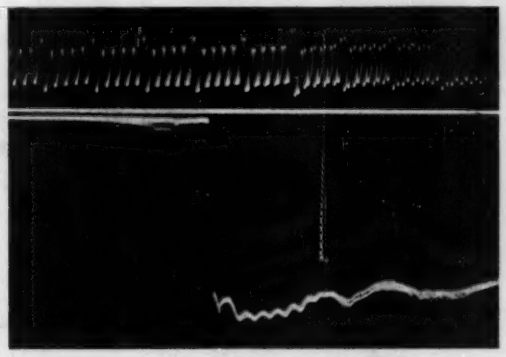


FIG 19
FUEL D1 INJECTION −30°

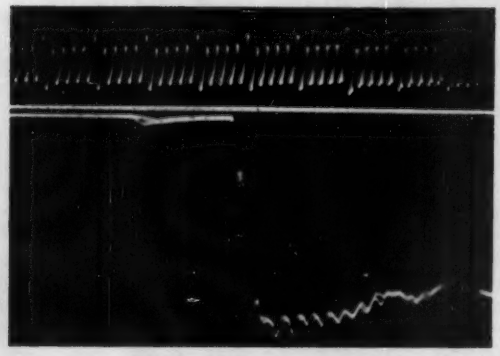


FIG 20
FUEL D1 INJECTION −40°

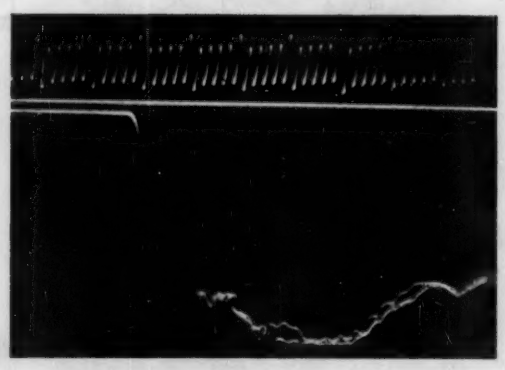


FIG 21
FUEL D1 INJECTION −45°

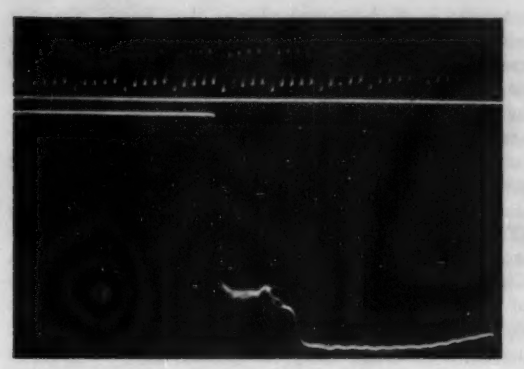


FIG 22

FUEL D1 INJECTION −50°

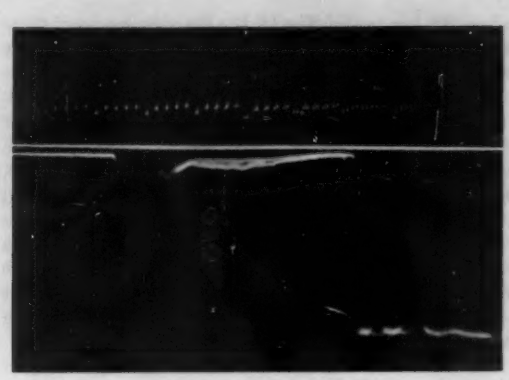


FIG 23

FUEL D6 INJECTION +10°

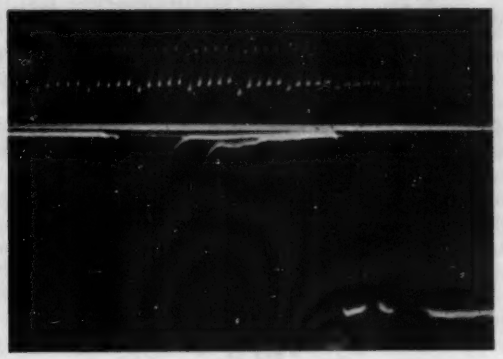


FIG 24

FUEL D6 INJECTION +5°

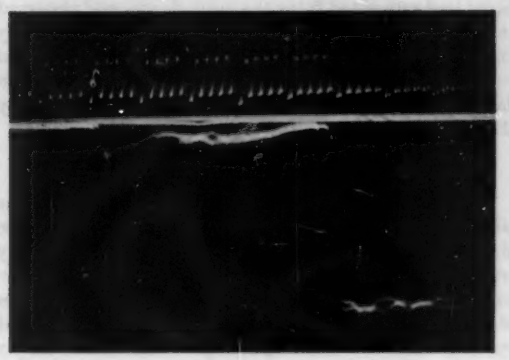


FIG 25

FUEL D6 INJECTION −0°

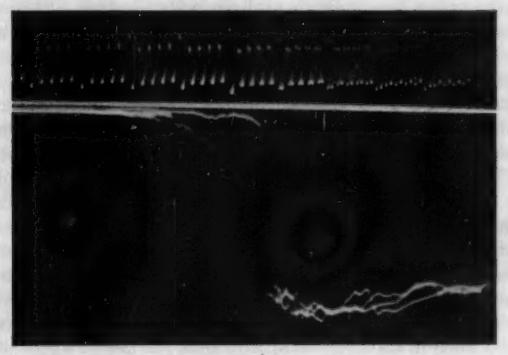


FIG 26

FUEL D6 INJECTION −5°

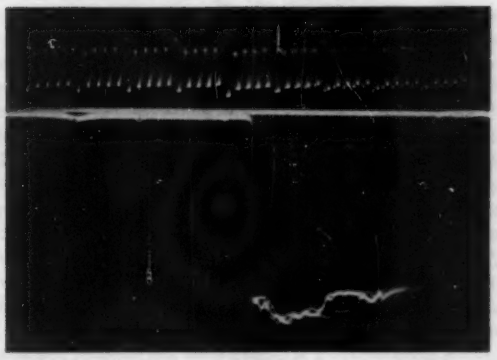


FIG 27

FUEL D6 INJECTION −10°

and +20° c.a.). In Fig 18 the smooth horizontal on the flame intensity curve shows that no pre-flame occurs (main flame at +4°).

FUEL D1

The flame intensity photographs for the high-cetane secondary reference fuel, D1, are shown in Figs 16–22. For an injection timing of +5° c.a. (Fig 16) a small intensity pre-flame occurred before injection of the fuel. As the injection was moved to earlier timings (Figs 17 and 18), the pre-flame was of very slight intensity at an injection timing of 0° (occurring at +4°) and had disappeared altogether at the injection timing of −5° c.a. (Fig 18).

Pre-flames were absent in the normal range of injection timings (−5° to −20° c.a.), but at early injection timings the pre-flames occurred again. In Fig 19 (injection −30°) the low intensity pre-flame occurred at −30°, merged with the main flame, and was accompanied by heavy knocking, as shown by the wavy trace of the main flame. At the earlier injection timing of −40° c.a. (Fig 20) the low intensity pre-flame had separated from the main flame, and occurred at the point of injection, accompanied again by heavy knock. As the injection moved earlier (−45° and −50°) the pre-flame again merged with the main flame, finally giving a step-like rise to peak intensity (Fig 22) and smooth combustion.

FUEL D6

The pre-flames occurring with the naphthenic gas oil, D6, appeared to differ in character from those obtained with the paraffinic fuel, both in intensity and position of occurrence. For later injection timings, +10°, +5°, 0° c.a. (Figs 23–25) pre-flames of high intensity occurred, the peak intensity being at approx −20° c.a. The pre-flames were followed by secondary peaks at t.d.c. This is shown particularly in Fig 25. The occurrence of these secondary pre-flames is discussed later with reference to their influence on the concentration of aldehydes in the combustion chamber.

With the more normal injection timings of −5° and −10° c.a. (Figs 26 and 27) pre-flames occurred, in contrast to fuel D1, which did not give rise to pre-flames at these injection timings. Fig 26 shows a pre-flame of varying intensity, appearing at −15° c.a. with a peak intensity at t.d.c. This pre-flame merged with the main flame in the step-wise manner observed with early injection of D1 (*cf* Figs 21, 22, and 26). At an earlier injection timing of −10° c.a. (Fig 27) pre-flames of low intensity occurred before injection at −30° c.a. and −18° c.a. accompanied by heavy knock. The heavy knock did not show in Fig 27 (*cf* Fig 20), as the main flame occurred after t.d.c. and not before as in Fig 20. Excessive knock occurred in the engine when operating on fuel D6 at injection timings earlier than −10°.

Both fuels show a similarity in the occurrence and position of low intensity pre-flames, which occur at or after injection, accompanied by heavy knock. This intensity is of the same order as that found in recent investigations into the precombustion reactions in a motored engine.[2,5] The intensity of the pre-flames occurring with late injection of D6 (Figs 23–25) would indicate that both the pre-flame and the main flame are similar in nature, the pre-flame being formed by unburnt fuel carried round from the previous firing stroke.

In the plot of ignition delay *v.* injection timing (Fig 15), the influence of pre-flames on the main flame is shown for both fuels, D1 and D6. At late injection timings, *i.e.* after t.d.c. for all fuel rates, the presence of the pre-flame is accompanied by an increase in the delay period. The occurrence of pre-flames at early injection timings temporarily arrests the gradual increase in the delay period as the injection timing moves to an earlier position.

SAMPLING EXPERIMENTS

Sampling Technique

On completion of the flame intensity measurements the adaptor tube was removed and the electromagnetic sampling valve fitted to the engine (Fig 1 shows the sampling valve in position). The larger volumes of gases withdrawn by the valve enabled a considerable modification in the sampling technique and methods of analysis described in the earlier paper.[1] In the present series of experiments separate samples were taken for aldehyde and peroxide analysis. After leaving the valve the gases were passed through a trap containing an absorbent, and the volume of gas was then measured by a gas meter (Fig 28). The trap was designed so that the outer tube containing the absorbent could be removed after sampling had been completed and the analysis carried out in the tube. The absorbent used for peroxide analysis was 5 ml of a 3 per cent aqueous solution of sulphamic acid which destroyed any nitric acid formed by solution of oxides of nitrogen in the gas. For the analysis of aldehydes the absorbent was 5 ml of a 0·5 M solution of sodium bisulphite. Preliminary experiments showed that 95 per cent of the peroxides and aldehydes were absorbed in the single trap and that the use of a second trap was unnecessary. For peroxide analysis sampling was continued until 10 litres of gas had passed

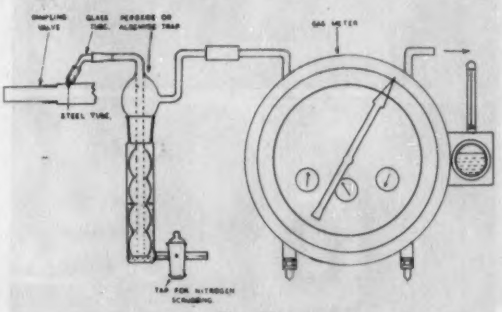


FIG 28

ARRANGEMENT FOR COLLECTING GAS SAMPLES

through the meter, whilst for aldehyde analysis a volume of 5 litres of gas gave a sample sufficient for analysis.

The increased rate of sampling also increased the scope of possible analytical methods. In the earlier work, colorimetric methods had to be used. For the present work, polarographic methods have been investigated, but so far have not proved satisfactory for the determination of peroxides. Titration methods were finally adopted as the most satisfactory for the present purpose.

Estimation of Peroxides

The potassium iodide method was used for peroxide analysis.[6] This method depends upon the reaction of the peroxide with the iodide in acid solution, in which iodine is liberated and then titrated with thiosulphate, using starch as an indicator.

In preliminary experiments on engine samples, treatment with potassium iodide produced no iodine, even after adding hydrogen peroxide to the sample. This suggested that iodine was being liberated, but that it was immediately removed by some other constituent in the sample. The two most likely constituents were sulphur dioxide, produced by oxidation of the sulphur in the fuel, and unsaturated hydrocarbons. Both types of compounds react readily with iodine. The interfering substances were removed by adding bromine water to the sample before analysis, and excess bromine was then absorbed with phenol. After this treatment, iodine was liberated when potassium iodide was added. Experiments on the effect of the length of the reaction period showed that there was no increase in the quantity of iodine liberated after the sample had stood for 2 hours.

Stock solutions of hydrogen peroxide, benzoyl peroxide, and tertiary butyl hydroperoxide were prepared and standardized, to check the accuracy of the method. The results indicated that if all the peroxide present in the engine samples was hydrogen peroxide, the error in values of the absolute concentration would not be great. If, however, large quantities of alkyl or aryl peroxides, *e.g.* tertiary butyl hydroperoxide, were present, the observed concentrations will be much smaller than the true values. The magnitude of the error will thus depend on the proportion of alkyl peroxides in the samples. The relative errors for the same type of peroxide are not so great, not exceeding ± 10 per cent. Thus, although the peroxide concentrations determined in later experiments have little absolute significance, their relative values are reliable.

Estimation of Aldehydes

The aldehydes were collected in a bisulphite solution, allowed to stand overnight, and were analysed by the method of Lea.[7] The excess bisulphite was titrated with iodine, and the aldehyde bisulphite complex then decomposed by addition of alkali. The quantity of aldehyde was then determined by titration of the liberated bisulphite with iodine. The rate of decomposition of the aldehyde bisulphite complex increases with increase of pH of the solution. Lea recommended the addition of sodium bicarbonate to raise the pH of the solution to 8·0. It was found that this was not sufficiently alkaline to ensure rapid decomposition of the complex, thus causing fading at the end point. This was avoided by making the solution more alkaline by the addition of sodium carbonate.

The aldehyde method was checked with standard solutions of formaldehyde. The error at the higher concentrations, 300 p.p.m. and above, was of the order of -10 per cent, but at lower concentrations, *e.g.* 50 p.p.m., the error was -3 per cent. In all cases, the reproducibility was ± 3 per cent.

ANALYTICAL RESULTS

Sampling experiments were performed over a wide crank angle span, before and after injection, for comparison with the flame intensity photographs. The

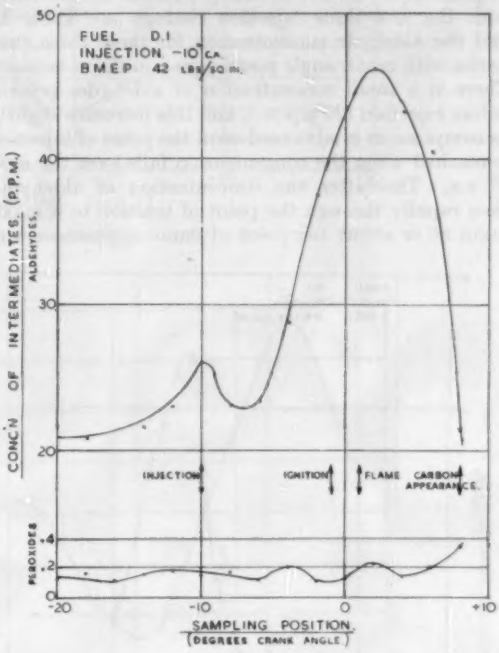


FIG 29

results of these experiments are presented graphically in Figs 29–35, in which the concentration of aldehydes (calculated as HCHO) and peroxides (as H_2O_2) are plotted against the crank angle position of sampling. It will be noted that aldehydes and peroxides are present in varying concentrations at all the crank angle positions sampled with or without the presence of pre-flames.

These results may be compared with the flame trace for corresponding engine conditions on the following basis. The flame trace results were obtained for a constant fuel input and variable load. On the Crossley engine, the load and fuel input cannot be varied independently, and the sampling runs were therefore

carried out at the same constant fuel input (26 ml/min) as the photomultiplier runs, this giving rise to different loads for the different fuels and injection timings. However, since for one fuel at one injection timing, the fuel rate and load is the same for both the sampling and the photomultiplier runs, the graphs of concentration of intermediates *v.* crank angle may be compared with the appropriate flame intensity photograph, although it may not be strictly correct to compare the results when a different injection timing is used.

To facilitate the discussion of these results, the points of injection, ignition, pre-flame, flame, and carbon appearance have been marked on each of the Figs 29–35.

FUEL D1

Figs 29–32 show the sampling results for fuel D1 at injection timings of −10°, −5°, 0°, and +5° c.a., respectively. With this fuel pre-flames do not occur with the first three injection timings (see Table V) and the aldehyde concentration for these three runs varies with crank angle position in a uniform manner. There is a small concentration of aldehydes present before injection (20 p.p.m.), and this increases slightly as compression is advanced until the point of injection is reached when the concentration falls over the next 4° c.a. Thereafter the concentration of aldehydes rises rapidly through the point of ignition to a maximum at or about the point of flame appearance and

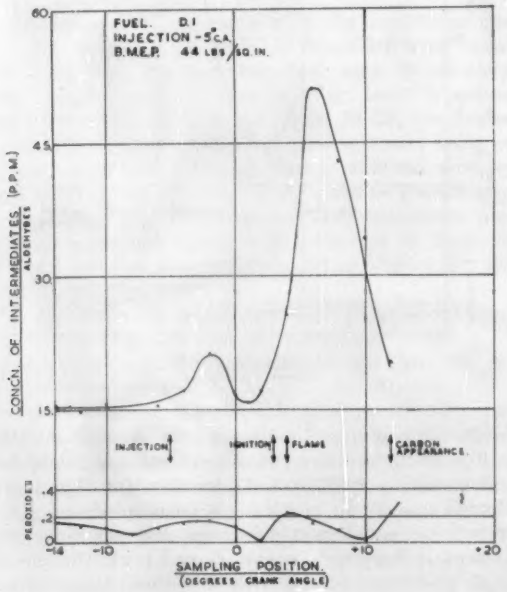


Fig 30

thereafter falls rapidly to the original value. The maximum concentration of aldehydes at flame appearance in these runs in which pre-flames do not occur is 60 p.p.m. (Fig 31). The peroxide content of the gases lies around 0·2 p.p.m. throughout the range tested, but

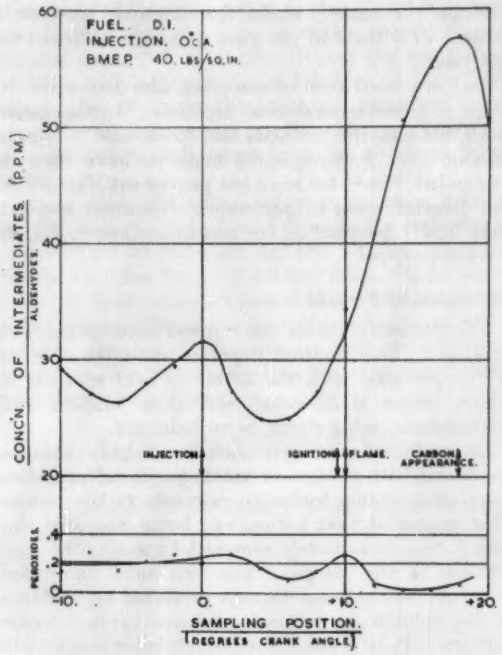


Fig 31

shows a slight increase at the point of flame appearance.

In the experiments with fuel D1 at injection timings of +5° C (see Figs 16 and 32) pre-flames were observed before fuel injection (−20° to +10° c.a.), and Fig 32 illustrates the marked increase in aldehyde concentration which accompanies the appearance of pre-flames. The aldehyde concentration at −20° c.a., the point at which the pre-flame commences, is 230 p.p.m., rises to a maximum of 380 p.p.m. at the pre-flame peak, falls off as the pre-flame proceeds, and then rises to a second peak about the point of injection. Thereafter, the concentration falls to the end of the pre-flame period but rises rapidly after ignition to a maximum of 440 p.p.m.

The peroxide concentration also shows an increase with the appearance of pre-flames, increasing from 0·2 to 0·6 p.p.m. in the pre-flame zone, reaching 1·2 p.p.m. in the period after ignition.

FUEL D6

Figs 33–35 give the results obtained with fuel D6 using injection timings of 0°, +5°, and +10° c.a., respectively, injection timings which give rise to pre-flames occurring before injection (Figs 23–25). Again the aldehyde concentrations are one-hundred-fold greater than those obtained with normal injection settings and in the absence of pre-flames.[1, Fig 14] In each case the aldehyde concentration increases from the point at which the pre-flame first begins to a position some 5° c.a. after the point at which the main flame appears, with intermediate peaks at the crank

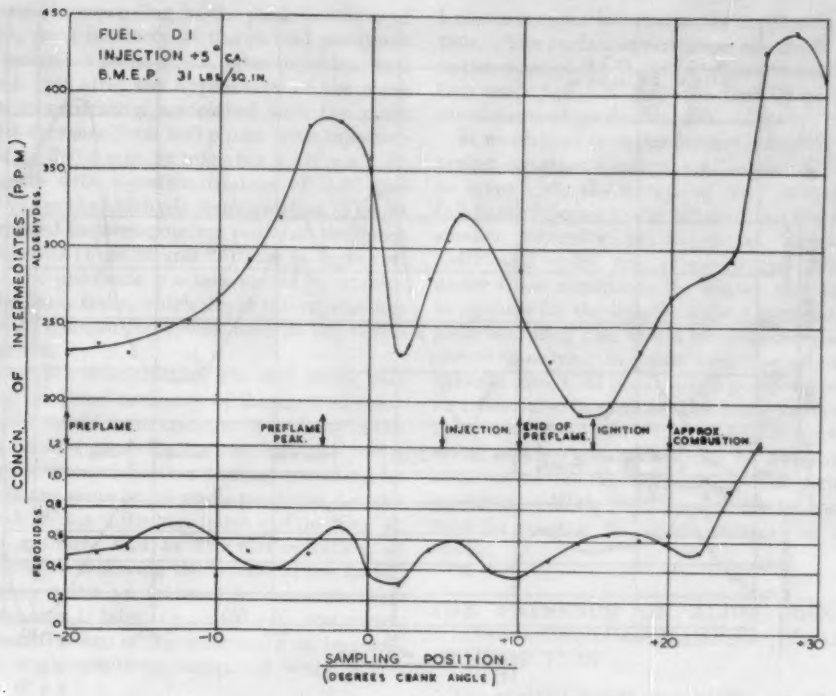

FUEL D1
INJECTION +5° C.A.
B.M.E.P. 31 LBS/SQ.IN.
CONC'N. OF INTERMEDIATES. (P.P.M.)
ALDEHYDES.
PEROXIDES.
PREFLAME.
PREFLAME PEAK.
INJECTION.
END OF PREFLAME.
IGNITION
APPROX COMBUSTION
SAMPLING POSITION.
(DEGREES CRANK ANGLE)

FIG 32

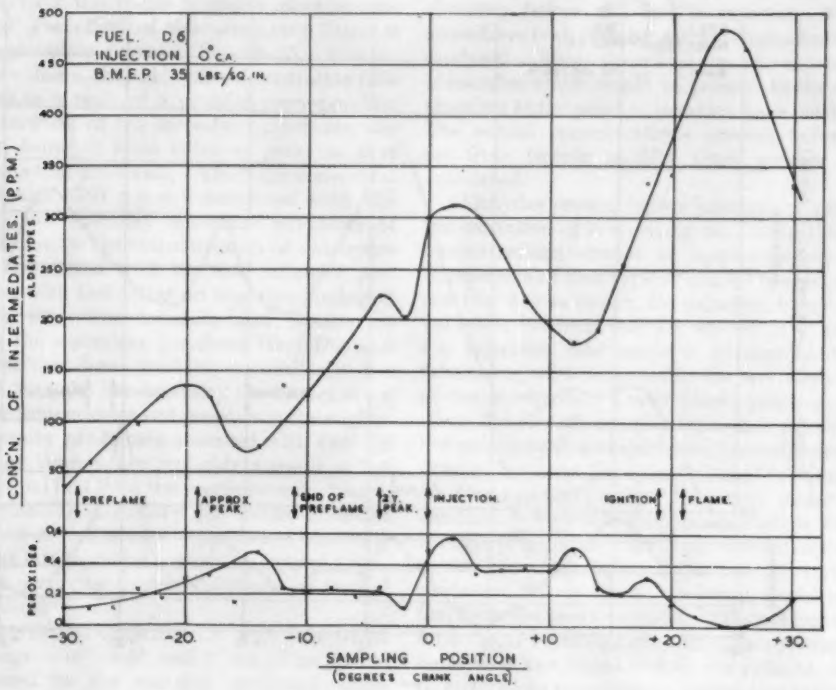

FUEL D.6
INJECTION 0° C.A.
B.M.E.P. 35 LBS/SQ.IN.
CONC'N. OF INTERMEDIATES. (P.P.M.)
ALDEHYDES.
PEROXIDES.
PREFLAME
APPROX. PEAK.
END OF PREFLAME.
2ND PEAK.
INJECTION.
IGNITION
FLAME.
SAMPLING POSITION.
(DEGREES CRANK ANGLE)

FIG 33

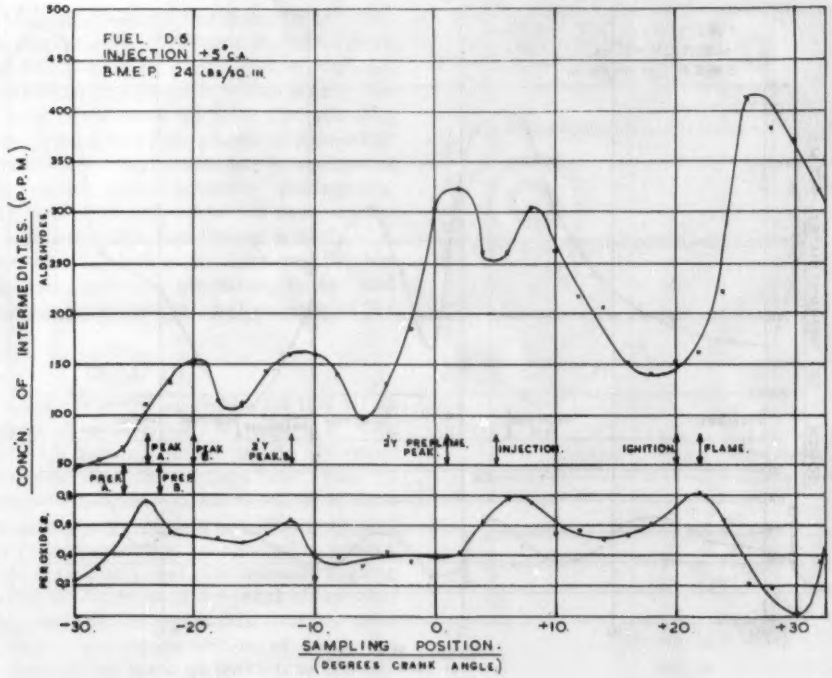

FUEL D.6
INJECTION +5° C.A.
B.M.E.P. 24 LBS/SQ. IN.
CONC'N. OF INTERMEDIATES. (P.P.M.)
ALDEHYDES.
PEROXIDES.
PEAK A.
PEAK B.
2Y PEAK.
2Y PREFLAME PEAK.
INJECTION.
IGNITION.
FLAME.
PREP A.
PREP B.
-30.
-20.
-10.
0.
+10.
+20.
+30
SAMPLING POSITION.
(DEGREES CRANK ANGLE)

FIG 34

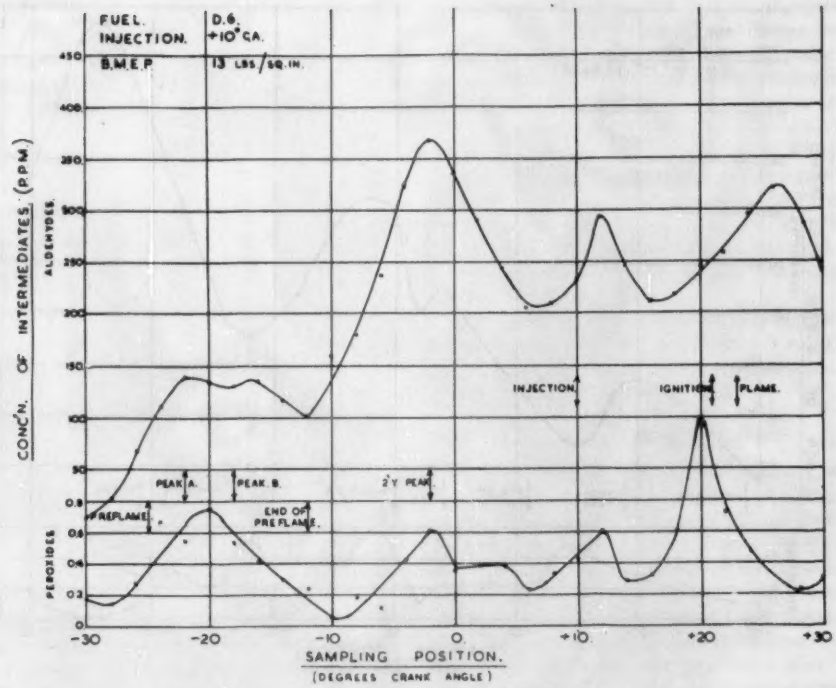

FUEL INJECTION. D.6 +10° C.A.
B.M.E.P. 13 LBS/SQ. IN.
CONC'N. OF INTERMEDIATES. (P.P.M.)
ALDEHYDES.
PEROXIDES.
INJECTION.
IGNITION.
FLAME.
PEAK A.
PEAK B.
2Y PEAK.
PREFLAME.
END OF PREFLAME.
-30
-20
-10
0.
+10.
+20
+30
SAMPLING POSITION.
(DEGREES CRANK ANGLE)

FIG 35

angle positions corresponding to the peak intensity of the pre-flame, peak intensity at the second pre-flame (where this occurs), a point 2° c.a. after injection, and finally a peak just after the appearance of the main flame. The concentration associated with the main flame shows a decrease from 500 p.p.m. with injection timing 0° c.a. to 380 p.p.m. at injection +10° c.a. In the experiments with injection timings of +5° and +10° two peaks in the aldehyde concentration (Figs 34 and 35) are related to corresponding peaks on the flame intensity diagrams (Figs 23 and 24). It is, however, possible that the pre-flame position varied by approx 5° c.a. and the flame trace, which shows the appearance for a number of consecutive cycles, records the variation as two peaks.

As the peroxide concentrations are very small, and in view of the predicted accuracy of the method mentioned earlier, it would seem ambiguous to draw peaks and troughs on the peroxide curves, but the peaks number four for every injection timing, occurring at approximately the same crank angle positions, *i.e.* the pre-flame peak, 2° c.a. after the point of injection, at the point of ignition, and as the concentration of aldehydes decreases following the arrival of the flame, so the peroxides show an increase in concentration. When the injection is later, *i.e.* +10° c.a., the corresponding concentrations of peroxide show an increase at all crank angle positions compared with earlier injection, *e.g.* 0° c.a.

The occurrence of a secondary pre-flame at t.d.c. with fuel D6 at late injection timings was mentioned in connexion with the flame intensity photographs (Figs 23–25). The effect of this secondary flame is shown in the sampling curves in Figs 33–35. Following the first pre-flame, the aldehyde concentration falls and then rises to a peak at a position corresponding to the peak position of the secondary pre-flame, the concentration being at least twice as great as that occurring at the first pre-flame. This high concentration of aldehydes (350 p.p.m.) associated with the comparatively low intensity secondary pre-flame of fuel D6, is similar to the concentration of aldehydes (380 p.p.m.) associated with the low intensity pre-flame observed with fuel D1 at an injection timing of +5° c.a. (Fig 32). The intensity and position of occurrence of the secondary pre-flame (fuel D6) and the low intensity pre-flame (fuel D1) are similar, and it would appear that the low intensity pre-flames are a function of the temperature and pressure in the engine. The high intensity pre-flames observed with fuel D6 at late injection timings are probably a result of hot ignition of residual fuel from the previous cycle, whereas the low intensity secondary pre-flames observed with fuel D6 and the low intensity pre-flames occurring with fuel D1 at late injection, occurring around t.d.c., are pre-flames occurring under conditions of limited fuel concentration.

When no pre-flames occurred, *i.e.* with fuel D1 at injection timings −10°, −5°, and 0° c.a. (Figs 29–31) carbon appeared in the samples, at crank angle positions which showed a sharp decrease in the aldehyde concentration and a rise in peroxide concentration. The carbon appearance, approx 8° c.a. after the appearance of the flame, was not noticed at an injection timing of +5° c.a. with fuel D1 or at any of the injection timings for fuel D6.

It was hoped to make further sampling runs at even earlier injection timings, *e.g.* −50° c.a. with fuel D1, to investigate the nature of the "step-like" rise to full flame intensity (Fig 22) and also the nature of the smaller intensity pre-flames at injection timings −40° and −30° c.a. (Figs 19 and 20). However, under these conditions the engine was knocking, and to operate for the length of time necessary for a complete sampling run would have meant damage to the sampling valve. Samples were also attempted on the exhaust stroke, at crank angle positions corresponding to those investigated on the firing stroke, but under these conditions either the exhaust or inlet valves were open, and no gas flow could be obtained from the combustion chamber under normal sampling valve operation. With suction applied to the system, it may be possible to obtain samples on the exhaust stroke.

THE PRESENCE OF ALDEHYDES IN THE COMBUSTION CHAMBER BEFORE FUEL INJECTION

The analytical data given in Figs 29–33 confirms the previous findings that aldehydes and, to a lesser extent, peroxides are present in the combustion chamber before the fuel is injected. The exhaust gases from both fuels for several engine loads have been analysed. From these analyses the concentrations of aldehydes which would be present in the combustion chamber at the point of injection have been calculated. The actual concentrations present before injection are from twenty to fifty times greater than those calculated.

Aldehydes present before injection might arise from the oxidation of lubricating oil, but in this event the concentrations should be approximately the same irrespective of fuel type or engine operation. This is not the case as shown, for instance, by the very wide variation between fuel D1 at −5° c.a. and at +5° c.a. injection, and hence it is improbable that the lubricating oil is responsible for any large proportion of the aldehydes. Under ideal operating conditions, when the fuel efficiency is high, it is possible that the low concentration of aldehydes present before injection does in fact arise from oxidation of lubricant film left on the cylinder walls. However, under operating conditions of lower fuel efficiency, such as late injection timings (Figs 32–35), the high concentrations of aldehydes occurring before injection are owing to the oxidation during the compression stroke of unburnt fuel from the previous cycle. It is not certain in what form the unburnt fuel remains in the cylinder. It may be present as a liquid film on the cylinder walls owing to incomplete vaporization during late injection of the fuel, or possibly as spray; again it may be partly

oxidized or polymerized, rather than unchanged, hydrocarbon fuel.

The small contribution of lubricant to the aldehyde concentration has been confirmed by operating the engine on an eight stroke cycle to give a double scavenging of the cylinder. Fuel was injected every four crankshaft revolutions. Samples were taken from the combustion chamber, over a range of crank angle positions from before injection to the time of flame arrival, both on the firing cycle and on the "dead" cycle, *i.e.* when there was no fuel injection. Under these conditions the engine could be operated only with fuel D1 at the normal injection timings of −8° to −10° c.a., timings which under normal four stroke operation do not give rise to pre-flames. With fuel D6 the engine could not be operated on an eight stroke cycle. The results obtained with fuel D1 proved that small amounts of aldehydes were present in the engine gases on the compression stroke of the "dead" cycle, but the quantity was less than 10 p.p.m. It would appear, therefore, that although a small amount of oxidation products (aldehydes) does arise from the lubricant, and will be present in the combustion chamber at the point of fuel injection, the larger quantities found under pre-flame conditions arise mainly from the oxidation of the fuel particles left from the previous cycle.

DUAL NATURE OF REACTIONS DURING THE DELAY PERIOD

It is well established that in the vapour-phase oxidation of hydrocarbons, oxidation reactions occur at temperatures below those required for spontaneous ignition. Townend [8] has shown that the spontaneous ignition diagrams for most hydrocarbons (exceptions are methane, benzene, and cumene) exhibit two main regions, a low temperature region (*ca* 400° C) and a high temperature region. Recent work suggests that methane [9] and benzene,[21] may have a low temperature oxidation process. Ignition in the low temperature region has been found to occur by a two-stage process involving the formation of peroxides and the presence of cool flames, whilst ignition in the high temperature region is by a single stage process in which peroxides play little part and cool flames are absent. Fallah, Long, and Garner [10] made a study of the vapour-phase oxidation of *n*-heptane, and reported maxima and minima in the curves obtained by plotting peroxide and total aldehyde and ketone concentrations against temperature. A similar phenomenon was found by Chamberlain and Walsh,[11] which was correlated with the lobes in the cool and hot flame limit diagram obtained by Maccormac and Townend.[12]

The occurrence of cool flames before hot ignition has been demonstrated in motored engines for a variety of hydrocarbons by many investigators.[13–17] Two types of pre-flames have been demonstrated, a cool flame, in which the emitter may be excited formaldehyde, and a blue flame, the exact nature of which is at present little understood. Downs, Street, and Wheeler [2] have made an exhaustive study of the occurrence of cool flames in a motored engine using visual observations and ultra-violet spectral analysis. Cool flames occurred with those hydrocarbons exhibiting a low temperature region in the spontaneous ignition diagrams.

Carhart [18] has reviewed the literature on this subject and suggested the following scheme of combustion for hydrocarbons. Assuming that the temperature necessary for ignition prevails in a gaseous mixture containing oxygen and hydrocarbon molecules, a series of reactions of chain-branching type will be initiated. The speed with which these reactions occur will depend on the temperature and the nature of the system, and the character of the container. The chain-branching reactions are not instantaneous, since a portion of the chain reactions which do start are broken by chain breaking reactions with the wall of the vessel, etc. For these reasons a time lag occurs between the beginning of the oxidation and the point where sufficient heat is liberated to ignite the whole mass. If the temperature is high enough the rate of intermediate formation is greater than the rate of destruction, and when a critical concentration is reached ignition occurs. The time necessary to reach this critical concentration is the chemical ignition delay period. However, under certain conditions, such as deficiency of oxygen, a cool flame may occur. The cool flame may burn and die out, it may be followed by a second cool flame after a second delay period, or it may be followed immediately by a hot flame. There is good reason to believe that a hot flame must always be preceded by a cool flame, but the latter is seldom observed under normal engine conditions because the time interval between the cool flame and hot ignition is so short. However, under borderline conditions for hot ignition, such as in a motored engine, the time interval between cool flame and hot ignition can be observed and measured.

These conditions exist in the diesel engine when the fuel injection is too early or too late for good operation. With early injection, ignition is delayed because the temperature of the air is not high enough to cause spontaneous ignition. Under these conditions the engine operation is rough and noisy, and fuel is lost owing to wetting of the cylinder walls and piston head. This results in poor fuel economy and smoke in the exhaust. With late injection, particularly after t.d.c., the fuel is injected late into the firing stroke, and again incomplete combustion of the fuel results. The experimental results given in Tables IV–VIII show that under these conditions the increase in delay period is accompanied by pre-flames, and the pre-flames are associated with very high concentrations of aldehydes (Figs 32–35). The character of the fuel is of importance in determining both the intensity of the pre-flame and the position of occurrence. With the high cetane number paraffin fuel, D1, pre-flames of low intensity occur at or after the point of injection for early and for late injection timings, and at very early injection timings, the pre-flame merges in a step-like manner with the main flame. With the low cetane

number, naphthenic fuel, D6, pre-flames of high intensity occur before injection with late injection timings, and these pre-flames are followed by secondary pre-flames associated with very high concentrations of aldehydes. With normal injection timings, $-5°$ and $-10°$, slight pre-flames, of low intensity, occur before injection (at 13° for injection at $-5°$ c.a. and $-30°$ and $-20°$ for injection at $-10°$ c.a.).

Further investigation of the character of these pre-flames is necessary, but it would seem that in the case of the paraffinic fuel, the fuel is completely or almost completely burnt in each cycle even at late injection, and that the pre-flames of low intensity are in fact cool flames formed during the initial oxidation of the fuel at temperatures below those necessary for hot ignition. With the naphthenic fuel the combustion is incomplete, markedly so at late injection timings, and the first pre-flames of high intensity are in all probability similar to the main flame, and represent hot ignition of unburnt fuel, or partially oxidized fuel, as the compression stroke produces the necessary temperature conditions for ignition. The secondary pre-flames which follow are possibly associated with oxidation under conditions of limited hydrocarbon concentration, and are similar to the pre-flames occurring with the paraffinic fuel at late injection timings ($+5°$ c.a.).

The concentrations of aldehydes observed in all cases in which pre-flames occur are similar to those observed by Downs and Wheeler [19] in the end gas prior to knock in spark ignition engines. The concentration of peroxides, however, is much smaller than that found by Downs and Wheeler and indeed smaller than that observed in the earlier work on the diesel engine, in which, however, much smaller samples were available and the analytical method not entirely satisfactory.

Accepting the current view that the chain carrier in hydrocarbon oxidation is a peroxy radical, the detection of only trace quantities of peroxides suggests that under the conditions of these tests in the diesel engine the peroxy radical is rapidly broken down into aldehyde or ketonic bodies. There is also the possibility that peroxy compounds are decomposed during the sampling procedure. The high concentrations of aldehydes suggest that the oxidation of the hydrocarbon at low temperature leads to a reaction in which aldehydes are formed, but that as the reaction temperature increases the aldehydes are further oxidized, ultimately to carbon dioxide and water. Thus, in normal operation (Figs 29–31) the aldehyde concentration is small, but rises as compression proceeds until the point of injection.

The injection of fuel seriously reduces the temperature and halts the oxidation of residual fuel or lubricant molecules. This is followed by a rapid increase in the concentration of aldehydes to the point of ignition when the aldehyde concentration falls rapidly. When the fuel is injected earlier, the increase in delay period permits a marked increase in aldehyde concentration to be achieved before hot ignition, and in those instances in which pre-flames occur, the pre-flame reactions appear to use up at least a portion of the aldehydes. Obviously, motoring the diesel engine, under cold starting conditions, for instance, would produce large quantities of aldehydes.

The work described is being continued by investigating the effect of compression ratio upon the occurrence of pre-flames, and by a study of the pressure changes in the combustion chamber for the various injection timings for which pre-flames have been detected. It is also hoped to extend the scope of the work by employing the improved analytical techniques developed by Pahnke, Cohen, and Sturgis [20] in their study of the chemical reactions occurring during knock in engines, and by the use of spectrographic methods [5] to establish the nature of the emitter in the two types of pre-flame and in the main flame.

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DISCUSSION

D. Downs: I am particularly pleased to have been asked to open the discussion on this paper, because I have long admired the work which Professor Garner and his team from Birmingham University have been doing in a difficult field. I and my associates have, over a period of some thirteen years, been carrying out a somewhat similar investigation into knocking combustion in the spark-ignition engine, using the sampling and allied techniques. Although our work is not without its difficulties, we are very conscious that it is an easier task than the comparable investigation in the diesel engine. In the petrol engine, for one thing, the mixture is more or less homogeneous. Additionally, we are not very interested in the normal combustion process initiated by the spark, but in the abnormal combustion which is liable to occur in the "end-gas," the last part of the mixture to burn, if the temperature–pressure–time conditions exceed certain critical values. In a given combustion chamber, the position of the "end-gas" can be determined, the chamber can usually be arranged so that the mixture is relatively quiescent, *i.e.* the "end-gas" stays in the same place throughout the cycle. Therefore, if a sampling valve is placed in the "end-gas," it can be used to follow the sequence of chemical reactions occurring in the reacting mixture prior to knock and the effect of engine and fuel variables on these reactions can readily be determined.

In the diesel engine, the position is very different. It is the normal combustion process, generally under the extreme conditions of high speed or cold starting, in which one is mainly interested, and this process is heterogeneous on both a micro and a macro scale. On what might be termed the micro scale, the local variations in mixture strength vary from all fuel to all air within the smallest possible space. This raises a difficulty in interpreting the results of sampling experiments because the products collected are the result of chemical interaction over a wide range of mixture strength, only a narrow band of which may be important, with the consequence that there is a risk of the significant products being masked by possibly larger concentrations of the insignificant.

Combustion is also heterogeneous on what might be termed the macro scale, because the sampling valve is fixed and the reacting mixture is in motion. High-speed photographs which we have recently obtained of combustion in the Comet chamber show that ignition usually occurs near to the wall, on the far side of the combustion chamber from the injector. Once ignition has started, the flame burns back along the fuel jet towards the injector and, at the same time, the whole reacting mass is swirled round in the opposite direction, *i.e.* away from the injector. These great movements of flame within the combustion chamber require one to be very careful in interpreting results which show two peaks in a flame intensity diagram against time. Whereas in the petrol engine it would be fairly safe to assume that these were consecutive events in the same body of "end-gas," in the diesel engine there is a probability that they are owing to successive waves of burning mixture passing the sampling valve. The curves of oxygen and carbon dioxide concentration against crank angle shown in the earlier paper of this series, as well as the similar curves produced by Egerton and Drinkwater for the same type of engine, suggest a combustion wave passing the sampling point at about 15° after top dead centre, and illustrate this point.

There is a further difficulty. From the fundamental point of view, one is presumably interested in the chemical reactions occurring prior to ignition to see how the latter can be linked with the former, and influenced by them. To do this properly, it would be necessary to place the sampling valve at the point in the combustion chamber where ignition first occurs. To place it anywhere else is to study not the reactions preceding spontaneous ignition but the passage of a flame front or of a swirling mass of burning gas, across a fixed position in the combustion chamber.

These considerations, which had no doubt also occurred to Professor Garner and his team, have always made me rather doubtful of the value of straight sampling experiments in the diesel engine. It is not too difficult to obtain results, the difficulty arises in interpreting them, and I am rather doubtful whether there is enough information to enable one to interpret the results which have been obtained in this series of experiments. To take first of all the light intensity diagrams. Are the pre-flames cool flames or hot flames? Are they caused by unburnt or partially burnt fuel in the residuals, by lubricating oil or by the fuel just injected? Recent experimental work has brought home to us the danger of attributing a low intensity C.R.O. diagram to a cool flame, *i.e.* chemiluminescence of excited formaldehyde, without further proof, as we have obtained a similar diagram in one case where chemically it was impossible for excited formaldehyde to be formed. So far as the lubricating oil is concerned, our motored engine experiments have shown flames owing to burning lubricating oil at compression ratios as low as 18 : 1. The characteristic C.R.O. diagram was, however, different from those shown in the paper. The intensity was higher, but the phenomenon more transient. Certain identification of the flame will be made only by spectroscopic examination, and I am pleased to note that this is a line which the authors intend to pursue in the future. I do not know whether at this stage they feel able to amplify the remarks they have made in the papers about the nature of these flames; at one point they seem to be considering them as low intensity normal flames and at another to be comparing the intensity, etc., with that of cool flames observed in other experiments.

The work seems to have established a rather nice agreement between flame development and aldehyde concentration, and I am wondering in what direction Professor Garner and his team propose to extend their investigation. I recall that in the preamble to the first paper read before the Institute in 1952, Professor Garner gave as his object the study of the pre-flame reactions occurring in the diesel engine with selected fuels, with and without the addition of ignition accelerators. I think that he had particularly in mind at that time an investigation of the reason for the often very different effects of ignition accelerators on cold starting and on normal combustion. I have already given some of the reasons why I think this will be very difficult to achieve with the present technique. I myself would prefer to carry out the investigation in a motored diesel engine with varying compression ratio, gradually increasing the compression ratio and analysing the products sampled at the point of ignition in the combustion chamber or in the exhaust, until ignition finally occurred. This would have the advantage of concentrating attention on the chemically important reactions occurring before ignition rather than on those occurring after ignition. Additionally, the much larger samples which could be obtained from the exhaust would increase the scope of the analysis. A certain amount of work has been done, I believe, by Professor Garner and his team along these lines in a CFR engine, and reported briefly in the previous paper. I should be interested to have the authors' present-day views on the relative merits of these two methods of approach.

From the fundamental point of view, diesel combustion problems occupy a sort of mean position between those of the spark-ignition engine and the gas turbine. In the former case, the limitations are largely chemical; in the

latter almost entirely physical. Although in the diesel engine the major combustion problems are perhaps physical, in the atomization and distribution of fuel throughout the combustion chamber, there are some problems, such as those of very high-speed combustion and cold starting, where the chemical component of the process becomes more important. Comparatively little work is being done in this field, and this makes it all the more important that there should be a research team in England, at the University of Birmingham, which is making a special study of this problem and gradually building up a large background of experience on the chemical aspects of diesel combustion. The authors will probably agree that only the fringes of the problem have, so far, been touched, and that very much more work needs to be done before one can fully understand even what has been done already. The industry is nevertheless very much in their debt, and it is hoped they will be encouraged by the interest which is being taken in their work to pursue it despite all the doubts and difficulties.

Professor F. H. Garner: We should like to express our appreciation of Mr Downs' comments, although it is difficult to reply to him in full detail immediately. His photographs show that the centre of ignition occurs near to the wall on the far side of the combustion chamber from the injector. It has to be remembered that most of our work is concerned with what happens before ignition, namely in the pre-flame region. Thus, interaction between the oxygen of the air and hydrocarbon will be proceeding simultaneously at a number of points until at one point, presumably because it is either just a little hotter or because the droplets are of the right size, ignition takes place. It is improbable that the pre-flame reactions proceed to completion at the point at which ignition takes place at any considerable length of time before elsewhere in the combustion chamber. In spite of the heterogeneity of the oil–air mixture there is a marked degree of uniformity in different cycles and good repeatability in all the various curves of oxidation products and flame intensity.

A comparison of the aldehyde and peroxide curves in the pre-flame and flame zones shows profound differences, and these should be considered in parallel with the flame intensity curves: it then appears highly improbable that the two peaks in the flame intensity diagram are the result of ignition. This point is quite important, since the character of the combustion products will obviously be quite different whether they take place as a result of air oxidation or as a result of combustion in the presence of a flame.

Professor F. Morton: Mr Downs' comments upon the heterogeneous character of the contents of the diesel engine cylinder, a point to which he referred in the discussion on our previous papers. We have satisfied ourselves, and make a brief reference to this in the paper, that variations in the position of the valve or the use of a different type of valve do not cause any significant variation in the sequence of events recorded in the graph of aldehydes and peroxide content *v.* crank angle position. It is surprising in view of the heterogeneous conditions that the results we have given are in fact repeatable. For any given fuel, injection timing, etc., the sampling curves are completely reproducible—even to the minor variations in peroxide content. It is this repeatability which has encouraged us to proceed with our investigations along the lines we have outlined.

We agree that the interpretation of the results is extremely difficult, but we believe that the sequence of events recorded at the sampling point is in fact the sequence of reactions, between pre-flame and main flame and that this sequence probably holds for all parts of the swirl chamber, although the time scale may be altered from point to point.

We have been careful to avoid stating that the observed pre-flames are in fact "cool flames" because we have not, as yet, attempted to identify the nature of the pre-flame. We think, without positive evidence, that in certain instances, notably with the low intensity pre-flames occurring at about top dead centre, the pre-flames are in fact cool flames, but this requires to be proven. We are, however, completely satisfied concerning the relationship between pre-flames and aldehyde concentration. Wherever pre-flames are observed they are associated with very high concentrations of aldehydes. Apparently, the pre-flames do not lead into hot ignition, nor are the high concentrations of aldehydes necessary for hot ignition, because with normal injection timings hot ignition occurs without pre-flames and with low concentrations of aldehydes.

We have, in earlier work, experimented with a CFR diesel engine under motored conditions. Although we might at some future date again use this technique, it was in fact abandoned because of the excessive corrosion which such an operation produces in the engine. We have, however, used the CFR engine to investigate the effect of compression ratio on pre-flames and pre-flame intermediates and hope to report this work in the near future.

Dr G. H. Grigg: In regard to Mr Downs' comments concerning the intensity of the pre-flames. From the work we have done so far with the Crossley and CFR engines, it is quite clear that when a pre-flame of high intensity occurs it does so before injection, whereas the low intensity pre-flames occur at or after the point of injection.

Dr H. B. Wiener: I would like to ask the authors two chemical questions. First, have they considered the fact that the pre-flame goes out in the light of ignition limit diagrams? Do they attach any significance to the fact that they get pre-flames only with early injection, when the pressure is increased after the pre-flame has started, and with late injection, when the pressure is decreased?

Secondly, do they consider their samples are large enough to be dealt with by gas analytical methods, so that one could take a few fractions and really give them the "works" on vapour-phase chromatography and all those new methods that have sprung up in the past few years.

May I finally make the innocent suggestion that they could put a tracer in their lubricating oil to see whether any of the products do, in fact, come from it.

Dr W. D. Reid: Perhaps I can deal with the second point, concerning the use of other methods of analysis of these gases. We have, as a matter of fact, tried the polarographic method, and in a small way, chromotographic methods. In regard to the use of the polarograph, there have been several papers published about the use of the polarographic method to detect peroxides and aldehydes in diesel engine exhausts, but we found that there were too many products masking the actual polarographic curves for us to make any reasonable analysis from them. In the case of the aldehydes, we did get a small wave due to formaldehyde, and then another large wave which was due presumably to a mixture of the higher aldehydes and possibly ketones. In the analysis of the peroxides, the presence of hydrogen peroxides was noticed, but alkyl peroxides were masked by the nitrates present in the sample solution. The same thing applies to any method of chromotography which one might apply to these samples, because there seem to be so many types of compound—aldehydes and peroxides—that actual analysis of each one is extremely difficult.

Professor F. Morton: In regard to Dr Reid's comments, may I add that we are hoping to use vapour-phase

chromatographic methods in the near future. Regarding Dr Weiner's suggestion concerning the disappearance of the pre-flame and ignition limit diagrams we have considered this point. At very high compression ratios in the CFR engine the low-intensity pre-flame appears to disappear at t.d.c. and reappear almost immediately. This may be owing to a peculiarity of the engine, but it has given us reason to think in terms of ignition limiting pressures, although we have not so far made any detailed study of this point. We have also considered the use of tracer elements in the lubricant, but have not yet evolved a technique for this purpose. We believe the facts given in the paper indicate that the contribution of the lubricant to pre-flame reactions is small.

Dr H. B. Wiener: Could I just repeat this question as to the quantity of sample? If one has as much as a litre, and one is getting 500 p.p.m. of aldehydes, one has half a c.c. at atmospheric pressure, and one could do some sort of fractionation with the Ward still type of apparatus, and that might make analysis a little easier.

Professor F. Morton: Yes, that is quite true, except that as I say we have not proceeded beyond the point of doing the simplest estimation that we could, in order to obtain as many sampling runs as possible.

Professor F. H. Garner: The analysis of the combustion samples is very difficult, and we have not found a reliable method of distinguishing between hydrogen peroxide and organic peroxides. In polarographic methods, peroxide of nitrogen coincided with one of the aldehyde peaks, and this made it difficult to apply this method for combustion products from internal combustion engines.

N. P. W. Moore: The work of Professor Garner and his group at Birmingham University is of particular interest to us at Imperial College. We have also been engaged for some time in an experimental study of pre-flame reactions in an engine. The work at Imperial College could be said to lie midway between the Birmingham work in a running diesel engine and the work of the Ricardo group (discussed by Mr Downs) in a running spark-ignition engine. Our work has extended the motored engine method to a compression ignition engine with an open combustion chamber and a compression ratio of 14·7 : 1. A very weak mixture of methane in air was pre-heated and passed to the engine with the subsequent pre-flame reactions studied both by gas analysis and spectrographic analysis. Methane was chosen as the fuel in order to simplify the analytical procedure and to obtain data in an engine to compare directly with experiments in static and flow systems on a laboratory scale. It was found possible to run the compression ignition engine under these conditions for long periods without apparent harm to the engine.

Our own work on the pre-flame oxidation of lean mixtures can be compared directly with the Birmingham experiments, in which a pre-flame reaction is detected before injection, presumably involving fuel (by this time evaporated) carried over from the previous cycle. A well-defined zone of pre-reaction has been established for weak mixtures and has been shown, even with methane, to involve the "cool flame" type emission of excited formaldehyde superposed on a background of burning carbon monoxide. Chemical analysis has shown the formation of carbon monoxide and its subsequent reaction at a later stage in the reaction when the methane is almost completely consumed. We have formed the view that at least with methane the pre-flame processes to give excited formaldehyde can take place only in the presence of reacting carbon monoxide. This has been confirmed in a simple flow system at atmospheric and low pressures.*

In discussing engine pre-flame data in the light of established laboratory scale experiments, it is most important to consider the particular temperature–pressure–time history of the charge in the engine. A recent determination of the spontaneous ignition limits of methane and propane in an engine has shown a remarkable similarity of behaviour despite their very different properties in a bomb or flow experiment with long induction periods.

It would seem to be a matter of great interest to learn more about the type of pre-flame reactions detected in the Birmingham experiments, and if possible to establish the nature of the emission by spectrographic analysis.

Professor F. Morton: We are all very interested in Dr Moore's comments and in the excellent work which he and his colleagues are carrying out at Imperial College. I am not sure, however, that one can extrapolate, as it were, from the results with methane to results obtained with a complex mixture of hydrocarbons of molecular weight around 300 and containing quaternary, tertiary, and secondary carbon atoms. The suggestion that the pre-flame in the methane–air reaction is in fact a cool flame and requires the presence of carbon monoxide for its occurrence is extremely interesting and is a point which we shall certainly follow. Our objectives are, however, perhaps different from those of Dr Moore and his colleagues. Although our results to date, and certainly those presented in the paper, deal with a diesel engine operating under unusual conditions, our primary interest is in the sequence of events in a diesel engine operating under ideal conditions. In this case, we are anxious to establish whether or not pyrolysis of the fuel occurs before or after oxidation. Our present study involves conditions in which oxidation precedes pyrolysis, but it is not established that this pre-flame oxidation leads to hot ignition unaccompanied by breakdown of the hydrocarbon. My personal opinion is that in normal conditions pyrolysis accompanies hot ignition, and may even precede it.

Dr W. T. Lyn: There are three points I would like to raise. The first has been dealt with at some length by Mr Downs. Four years ago, when the authors presented Parts I and II of the investigation, I raised the point that care has to be taken in interpreting the results of sampling tests obtained from a diesel engine. Owing to the heterogeneous characteristics of diesel combustion, the original air–fuel ratio of the sampled portion varies widely. This undoubtedly has considerable influence on the partial products, as in the subject of investigation in the paper. The authors could easily determine the local air–fuel ratio by burning the whole sample in an external furnace and subsequently determining the CO_2-content. I have done some work of this nature in connexion with the study of fuel distribution when I was at the BICERA laboratories in Slough, and Fig A shows a typical result obtained from a Crossley BWI engine of practically the same design as the one used by the authors, but of a slightly larger size. In order to use an uncooled sampling valve so as to reduce the valve size, the engine was motored and a high ignition temperature fuel was injected so that no combustion takes place in the engine. The sample of air–fuel mixture was burned in a tube furnace before the products were passed through a CO_2-recorder. Although the experimental condition is not exactly comparable to those used by the authors, there are sound theoretical reasons to believe that the first order pictures are the same. It is interesting to see that the local mixture ratio varies considerably and in the centre of the

* Gaydon, A. G., and Moore, N. P. W. *Proc. roy. Soc. A* (in the press).

chamber it has never reached 60 per cent of stoichiometric ratio. This means that a considerable portion of the charge is below the lower limits of inflammability at the centre of the chamber.

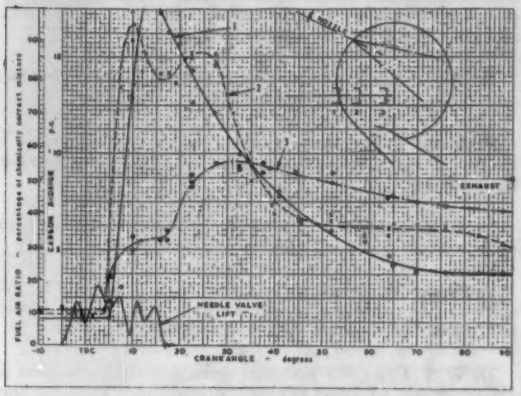

FIG A

MIXTURE DISTRIBUTION IN COMBUSTION CHAMBER WITH THREE POSITIONS OF VALVE

870 rev/min, 6·6 lb/hr fuel flow, and 120 atm nozzle release press.

A proper interpretation of the author's results should really include (*a*) the original air–fuel ratio, which, as I said earlier, can be obtained by burning all the samples outside the engine, and (*b*) the CO_2-curves from the engine, like those obtained by Egeton and Drinkwater. These two curves will give the degree of completeness of combustion of that particular portion of the charge at that particular time. Comparison of the author's result with curve (1) of Fig A shows that the appearance of aldehydes and peroxides correspond to a region where the original air–fuel mixture is over rich, as is to be expected. Incidentally, Professor Morton's reply to Mr Downs' criticism is not really tenable when he said that by moving the sample valve a $\frac{1}{4}$ inch into the chamber he still got the same result. The explanation of this is that the time variation of the original mixture ratio is the same for these two positions, as can be seen from Curves 1 and 2 in Fig A, but it does not mean that they are uniform. The results presented in the paper may be interpreted as the history of the occurrence of successive events in the engine only when the original mixture ratio is uniform, as in the case of petrol engines. In the case of diesel engines, each sample taken at a particular crank angle is from a particular element of charge having a particular residential time in the engine.

In regard to the small acceptance angle of the photocell, the $3\frac{1}{4} \times \frac{1}{4}$-inch passage would drastically reduce the view of the cell to almost a pencil line. Would the authors not consider such limitation makes the interpretation of the results difficult if not unreliable?

Finally, in Figs 29–35, the position of the occurrence of the ignition as distinct from flame was indicated but not explained. I suspect that this is the point where rapid pressure rise begins, but the authors stated that they have taken no pressure measurements.

Professor F. H. Garner: The distribution of fuel oil in the combustion chamber will probably be altered considerably by the insertion of the probe, particularly when it is at its most advanced position, and this throws some doubt on the analyses given on the slide. We do, however, feel that Dr Lyn's suggestion to determine carbon dioxide on some of the combustion samples is worth following up.

Professor F. Morton: Dr Lyn's comments are of considerable interest. We agree that measurement of local fuel–air would be of value, and we may possibly repeat some of our work using the technique suggested by Dr Lyn. The small acceptance angle of the photo-cell is to some extent deliberate, the intention being to cut out light from all sources except the point course at which sampling had been performed. The point of ignition is taken as that point at which the light intensity trace leaves the horizontal trace, and flame arrival as the point of maximum intensity of this trace. Pressure measurements have been taken and will be reported separately.

J. G. Withers: Might I ask the authors their views on the applicability of their conclusions to other engine designs? The authors used a swirl chamber engine, which undoubtedly is more likely to retain unburnt fuel from the previous cycle, since the swirl chamber is less thoroughly scavenged than the combustion chamber of a direct injection engine. I feel fairly certain that the pre-flames were a result of this unburnt fuel. I recall several experiments made some years ago on the same model of engine as the authors have used, when we were trying to determine the Cetane nos. of different fuels. The IP throttling technique was employed, and two discrete curves of limiting manifold depression against Cetane no. with a small period of overlap between them was obtained, as shown in Fig B. Between 40 and 50 Cetane no. there were two different levels of limiting manifold depression but there was never an intermediate one. At the time, this phenomenon was the subject of much

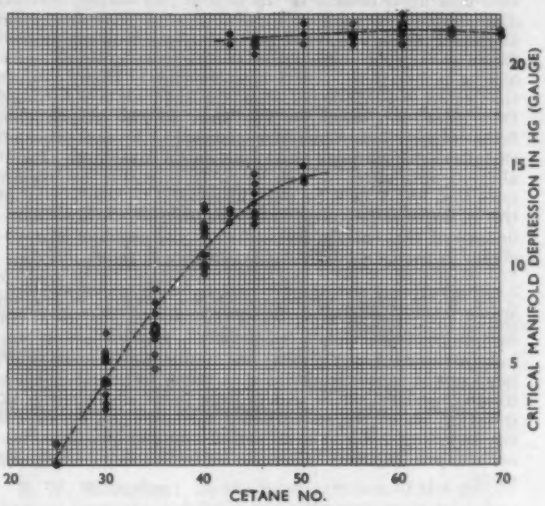

FIG B

I BVD CROSSLEY ENGINE (MISFIRING PRESSURE *v.* CETANE NO.) THROTTLING TEST

1500 rev/min, b.m.e.p. 10 p.s.i.

concern, but there would now seem to be no doubt that in one case it was owing to pre-flames, and in the other to no pre-flame. As one might expect, the pre-flames are induced by the rich mixtures resulting from high manifold depressions, associated with the upper curve. A similar effect was shown by a discontinuity in the curve of ignition delay *v.* injection advance, in which the ignition

delay suddenly shortened by 4° of crank-angle rotation as the injection was advanced beyond 11°.*

A number of experiments was also made with direct-injection engines, but this anomaly was never found. I therefore believe that the pre-flames observed by the authors are peculiar to the swirl chamber type of engine, and that in the direct injection engine they either occur at a much lower intensity or not at all.

Dr G. H. Grigg: I made reference to work which has been done on the CFR engine, in which we observed the pre-flames, but at very much higher compression ratios—in the region of 25 or over, with a normal fuel rating of 13 ml/min. The only types of engine we have investigated are the CFR and the Crossley. We obtained high and low intensity pre-flames with both engines.

J. G. Withers: Both the CFR and the Crossley engines are of the swirl chamber type and, as such, presumably have similar characteristics. We have operated a standard spark ignition CFR engine quite successfully as a direct injection diesel engine. The injector was located in the bouncing pin hole giving a spray across the axis of the cylinder. Although we did not go very far with this work, I believe it is possible to get quite a reasonable performance from the pancake type of direct injection chamber obtainable with the conventional CFR engine. This conversion might be a way of extending the scope of the authors' pre-flame investigations.

Dr E. B. Evans: One of the most interesting points in the paper concerns the appearance of carbon in the samples when using high cetane fuels and normal injection timings. That carbon does not appear if the injection is a little later. Is the amount of carbon formed appreciable? I take it that at the present stage the analytical methods do not permit an accurate estimation of the quantity of carbon, but what is the real significance of that carbon in the reaction mechanism? Do we assume that a pyrolysis of the paraffinic type of fuels is occurring? One does not seem to get that in the naphthenic fuels, which if I remember correctly, do not produce carbon in the samples at any period of injection. Probably at this stage of the work it is rather an unfair question, but I shall be very interested to hear if any of the co-authors has any views on what is the real significance of this carbon formation in the combustion process. It seems a particularly interesting point.

Dr W. D. Reid: In regard to the amount of carbon that is produced, it is sufficient to cover the surface of the sampling vessel with a thin film. That is about the only estimate I can give at the moment. We have not been able to measure it, as it is much too small—it is a micro quantity, but it is definitely there, and there is no question about the valve being carboned up, because if the sampling is taken to an earlier crank angle, no carbon occurs, proving that it is not due to the valve becoming dirty.

Professor F. Morton: In regard to the mechanism of carbon formation we have no real evidence, but we believe that pyrolysis of the hydrocarbons accompanies or possibly precedes hot ignition and that subsequent cracking reactions are responsible for carbon formation.

Dr E. B. Evans: Carbon formation occurs over the injection range from −10° to 0°, but at +5° injection no carbon is formed. I would have thought that the phenomenon would have persisted with later timings. What accounts for the disappearance of carbon formation?

Professor F. Morton: Is not this point comparable with Dr Lyn's question, *i.e.* dependent upon fuel–air ratios at a particular point. With late injection into a hot engine there is a greater rate of vaporization but a minimum time for vaporization before ignition. This could mean that combustion occurs in the vapour phase surrounding droplets already at a high temperature with subsequent cracking of the liquid–vapour fuel.

Dr E. B. Evans: Are you suggesting more, or less, vaporization in late injection?

Professor F. Morton: In the case of late injection, I think more, because vaporization follows injection immediately.

Dr E. B. Evans: In the case of a naphthenic fuel, no carbon at all has been observed?

Professor F. Morton: The amount formed is insufficient to cause a film of carbon in the sample vessels so that we have recorded it as no carbon formation.

Dr W. T. Lyn: My personal opinion is that pyrolysis is all important in diesel engine combustion. It is not the original fuel which is burned, but some solid intermediates formed by pyrolysis all the time. This is supported by the i.r. spectra which I have taken from diesel and petrol engines, as well as from some laboratory flames.

It is known, however, from published laboratory work that pyrolysis could take place at the temperature and within the time interval during the delay period. These experiments were done under atmospheric conditions. The high pressure under diesel conditions must greatly accelerate the pyrolysis process.

Professor F. H. Garner: In the paper we have suggested that the pyrolysis products will be present in the diesel engine as a result of cracking of the hydrocarbons, but in thermal cracking pressure has no influence in accelerating the rate of reaction, since it is a monomolecular reaction. The question of whether the oxygen attacks the hydrocarbon molecule or a radical formed from it, is a fundamental point. In the case of normal heptane we find that peroxides were formed at a temperature of 220° C in the vapour phase. At all events, if radicals are the starting mechanism, then oxygen must play a great part in continuing the general reaction process.

J. F. Alcock: In Figs 29 and 31 of the paper, there is a sharp dip in the aldehyde concentration curve, just before the rise which immediately precedes ignition. On p. 85 this is apparently ascribed to the cooling of the air by the cold injected fuel.

A difficulty about this explanation is that in Figs 29 and 31 the increase of aldehyde concentration starts to fall off immediately injection starts. With the normal swirl rate in this type of chamber (16 × crank rev/min) air, cooled by the incoming fuel, should take at least 3° of crank angle to reach the sampling valve, which is some 45° downstream of the injector. Thus, cooling, or any other influence of the incoming fuel, should not show up at the sampling valve until at least 3° of crank after the start of injection.

In Fig 29, too, the peroxide concentration starts to fall about 3° *before* the start of injection. Thus, the injection cannot be responsible.

The later *rise* of aldehyde and peroxide concentration does, however, occur 3°–5° after injection, and may be

* Wachal, A. L., and Withers, J. G. "Combustion Performance of a Swirl Chamber Diesel Engine." *Gas Oil Pwr*, 1950, Oct.

owing to the first reaction products of the injected fuel reaching the sampling valve.

Professor F. Morton: I am not entirely satisfied that swirl is the only mechanism by which the gases at the sampling point may be cooled by injected fuel. The rate of injection would spray fuel over the chamber and the droplets would have a greater speed than the moving air mass. As an alternative to cooling by the fuel there is a possibility of non-regenerative cross linking between aldehydes and fuel molecules as suggested by Ubbelhode, but we have insufficient evidence to confirm either mechanism.

Dr E. A. W. Austen: I should like the authors' views on a matter about which I am in some confusion and which I think may bear directly on the work we are doing on cold starting. It is whether the pre-injection pre-flames, or reactions of partial products in the pre-injection period, promote ignition, prevent it, or are without effect. I am not clear what the authors' view on this is.

I had hoped that the authors' eight-stroking experiments might shed some light on this point, and indeed I think there may be some evidence there. May I ask why the engine would not run except in a rather narrow range of conditions with the D1 fuel? Was it that the engine would not fire on other fuels? If so, this is already a quite significant result.

There is a rather surprising result in the eight-stroking experiments, in one of which (p. 86) there was an aldehyde concentration of 10 p.p.m. on the "dead" stroke. In the corresponding normal running experiment (Fig 29), the corresponding aldehyde concentration rose to about 25 p.p.m. Now it would be reasonable to expect a low pre-injection aldehyde concentration on the live stroke, since it is not preceded by a normal stroke. On the "dead" stroke the aldehyde concentration should be normal. I would, therefore, like to ask if there is any evidence on aldehyde concentration on the live stroke and also if there was any considerable difference in the delay period in the eight-stroking experiments as compared with the normal running.

Dr W. D. Reid: First, in regard to an engine running on an eight-stroke cycle, it is extremely difficult to get it to turn over at all. It is not a motored engine, it is running under its own power, and it would run only under certain injection settings, so that we could not vary the injection timings.

Secondly, there was some variation in the ignition delay from cycle to cycle, and it was rather difficult to obtain any reliable results under eight-stroking conditions. But we did find, in general, the ignition was not greatly altered.

Finally, in the sampling experiments, the presence of aldehydes and peroxides before the injections, *i.e.* at the end of the dead stroke, seemed to suggest that the lubricating oil was contributing something towards this. At that time, it appeared to us that those peroxides and aldehydes were purely from lubricating oil. On the other hand, they may have come from the oil remaining on the sides of the cylinder, or in the combustion chamber on the firing stroke.

Professor F. H. Garner: In regard to the effect of the small flame on the performance, I think that Dr Evans presented a paper some time ago, in which it was shown that the injection of a small amount of fuel before the main position helps considerably in promoting smooth ignition. This applies whether the fuel used is gasoline or diesel fuel.

Dr H. B. Wiener: I would like to ask one more analytical question. When one burns propane with a deficiency of oxygen, one gets a lot of unsaturated compounds. In the diesel engine presumably, with the paraffinic fuel, one also gets unsaturated compounds. I wonder if the authors have detected any, or looked for any, unsaturated compounds.

Dr W. D. Reid: We have never been able to detect any unsaturated compounds in the samples which we have taken from the sampling valve. We did take some samples from the CFR engine, very large gas samples, when it was being motored under various compression ratios; they were very large samples, 700, and we never detected any unsaturated hydrocarbon compounds there.

G. M. Barrett: I would like to refer once more to this question of eight-stroking, I think the authors state that with the low cetane fuel the engine would not run at all. That seems to imply that with a fuel of low ignition quality one normally relies for ignition on fuel carried over from the previous cycle. If the scavenging is too good, the engine will not fire. When one comes to consider turbo-charged engines, which have very good scavenging, one usually regards them as an application where fuel properties do not matter very much. Certainly they can burn heavier fuels, and I always imagined that they would burn low ignition quality fuels. However, if the theory of carry-over is correct one would expect that turbo-charged engines should misfire on fuels of very low ignition quality.

Professor F. Morton: I am not certain that Mr Barrett's conclusions are correct. It is true that the engine could not be operated on an eight-stroke cycle using a low cetane fuel, but it does not follow that the engine would not fire because there was no residual fuel present. The engine cools fairly rapidly and in the eight-stroke operation using a high cetane fuel the engine could operate only between very limited injection timings. The failure to fire with low cetane fuels may be due to the lower engine and combustion chamber temperatures.

A. E. W. Austen: One can probably check that by running a four-stroke at normal speed, and suddenly switching in the eight-stroke, and so one would get a continuance of the eight-stroke engine slowed down.

Dr W. D. Reid: Yes, that is exactly what does happen.

Lt-Col. S. J. M. Auld: The authors are to be congratulated on the high standard of their work and on the presentation of their paper. The interest in the subject has been clearly indicated by the discussion it has invoked —undoubtedly, the combustion of hydrocarbons in the diesel engine is a fascinating subject.

The meeting then closed with a warm vote of thanks to the four authors of the paper.

CONTRIBUTED DISCUSSION

B. W. Millington: In the interpretation of the graphs derived from the aldehyde analyses care must be taken to allow for the relative phasing of events occurring in different parts of the chamber. For instance, it is suggested that the reduction in aldehyde concentration at about the time of start of injection is due to the cooling effect of the fuel. This would seem to be rather unlikely. Fuel enters the chamber at the nozzle and crosses to the opposite side, impinging on the heat-insulated member of the chamber. From here spray and vapour are carried round the chamber near the periphery by the rotational air movement. From photographic observations it appears that the time lapse between start of injection and the arrival of fuel at the position of the sampling valve is of the order of 10 crank degrees. In view of the orderly

air motion in this type of chamber it would appear unlikely that appreciable cooling could occur near the sampling valve in a time interval less than this.

I would suggest that the decrease in aldehyde concentration at about t.d.c. is associated with the arrival at the sampling valve of clean air from the cylinder space. In this connexion it should be realized that the greatest transfer rate of air from the cylinder to the chamber is at about 20° before t.d.c., and allowing for a delay of about 8–10 crank degrees for this air to circulate from the throat to the sampling point, it will be seen that the highest concentration of clean air at the sampling point should be some time around 10° before t.d.c.

As I have said, the fuel first traverses the chamber and then is carried round with the air; by about 10° after start of injection when ignition first occurs the forefront of this fuel will be in the vicinity of the sampling valve. The first appearance of flame is to be seen as a rule some little way behind the fuel front and the flame then spreads forward to the front. It therefore appears that in the Crossley engine the sampling valve is sited in a position where it receives fuel that has had the longest resident time in the chamber and is in all probability largely vapour and through which a flame front travels in a manner akin to a spark-ignition engine.

The appearance of carbon later in the cycle I would associate with the arrival at the window of fuel that has ignited after a short resident time, combustion taking place at the surface of discrete droplets.

I am sure the authors are conscious of the fact that detailed studies of the combustion process at injection timings far removed from practical fuel injection timings may have little bearing on diesel combustion. After all, a swirl chamber engine of this type will run at any injection timing whatsoever on a good quality fuel, and if one injects, say, on the induction stroke, one would expect the mode of combustion to approach that of the spark ignition engine.

An interesting direct application of the tests described concerns the use of diesel engines in mines, where the presence of partial oxidation products in the exhaust gas is objectionable. Thus, the importance of using the correct injection timing, for instance, in this connexion is well brought out.

THE VAPOUR PRESSURE OF ALCOHOL–GASOLINE BLENDS*

By GEO. E. MAPSTONE†

SUMMARY

It has been shown that the increase of vapour pressure of alcohol–gasoline blends with temperature is not significantly different from that of other gasolines and, consequently, these blends should not be more susceptible to vapour lock than other gasolines of the same R.V.P. A nomograph is presented that allows the ready calculation of the Reid Vapour Pressure bomb correction for the dry bomb used for alcohol–gasoline blends.

INTRODUCTION

ALCOHOL–GASOLINE BLENDS are frequently accused of being more susceptible to vapour lock than are alcohol-free blends. Much of the difficulty appears to have been owing to early investigators, who compared the vapour locking tendencies of alcohol blends with that of gasolines of lower vapour pressure.[1,3] However, because of the relatively higher latent heat of evaporation of the alcohol it was suspected that the vapour pressures of alcohol blends would increase more rapidly with temperature than those of other gasolines. The data reported here show that these fears were groundless.

The most convenient method available for determining the vapour pressure of a gasoline is the Reid method (ASTM D323–52; IP 69/55), which is modified by using dry equipment when applied to alcohol blends, as otherwise the water deliberately present will cause phase separation and erroneous results. With alcohol blends, therefore, the correction for the expansion of the air in the chamber is different from that when the usual wet bomb is used.

CHART FOR CORRECTION FACTOR

The R.V.P. correction factor is given by the relationship $C = [P\ (t - T)]/460 + t$

where C = Pressure correction in p.s.i.;
P = Barometric pressure in p.s.i.;
t = Initial air chamber temperature °F;
T = Bath temperature °F.

The accompanying nomograph (Fig 1) allows this correction to be calculated very simply and allows ready adjustment for both barometric pressure and for changes in the bath temperature which may be required and which are allowed by IP 69/55.

EFFECT OF TEMPERATURE ON VAPOUR PRESSURE OF ALCOHOL BLENDS

Because of the relatively high latent heat of evaporation of alcohol it may be expected that the vapour pressure of alcohol blends would increase more rapidly with temperature than in the case of alcohol-free blends. In order to check on this assumption the data in Table I were obtained, and plotted in Fig 2 on the nomograph previously derived [2] for the variation of the vapour pressure of gasolines with temperature.

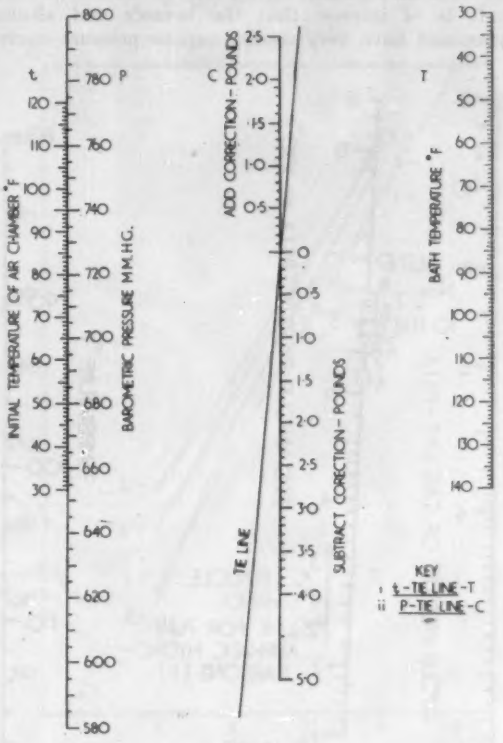

FIG 1

NOMOGRAPH FOR CORRECTION FOR R.V.P. OF ALCOHOL–GASOLINE BLENDS

It can be seen that the six alcohol-containing blends examined and containing from 5 to 30 per cent of alcohol by volume show a negligible deviation from the line for alcohol-free gasolines. This means that the vapour pressures of alcohol blends do not increase faster than those of alcohol-free blends and,

* MS received 12 December 1955.

† South African Torbanite Mining and Refining Co. Ltd.

TABLE I

Vapour Pressures of Alcohol–Benzole–Gasoline Blends

Blend No.	Composition			Vapour Pressure				
	Gasoline	Alcohol	Benzole	80° F	90° F	100° F	110° F	120° F
1	100	—	—	5·5	6·6	7·6	8·9	10·4
2	90	—	10	5·3	6·4	7·3	8·5	9·9
3	80	—	20	5·2	6·2	7·2	8·5	9·7
4	70	—	30	4·5	5·4	6·1	7·3	8·8
5	—	—	100	1·4	2·0	2·7	3·6	4·7
6	90	10	—	6·2	7·5	8·6	9·9	11·5
7	80	20	—	5·8	7·2	8·4	9·6	11·2
8	70	30	—	5·7	7·1	8·2	9·5	11·0
9	—	—	10	1·5	2·1	2·9	3·5	4·5
10	90	5	5	5·4	6·7	7·9	9·2	10·7
11	80	10	10	5·5	6·7	7·9	9·2	10·7
12	70	15	15	5·5	6·6	7·9	9·1	10·7

consequently, would be no more susceptible to vapour locking troubles than other gasolines of the same R.V.P. (at 100° F).

It is of interest that the benzole and alcohol examined have very similar vapour pressure curves

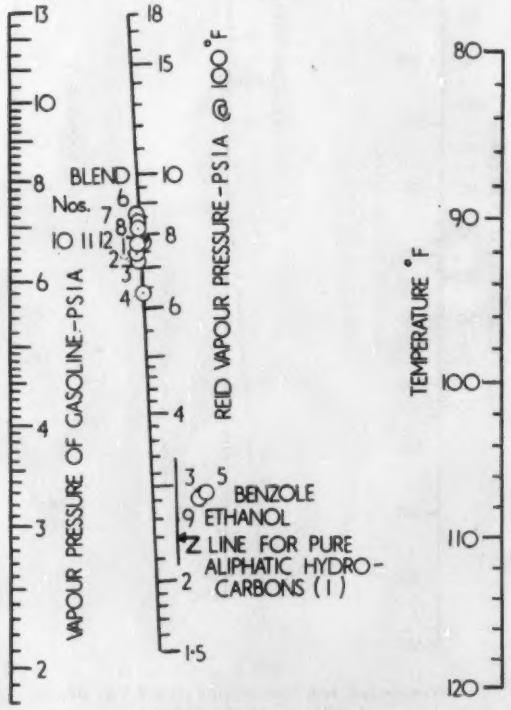

FIG 2

NOMOGRAPH FOR EFFECT OF TEMPERATURE ON VAPOUR PRESSURE OF GASOLINE

and appreciably higher relative latent heats of evaporation than either gasolines or pure aliphatic hydrocarbons. A portion of the line for pure aliphatic hydrocarbons is given in Fig 2 for comparison.

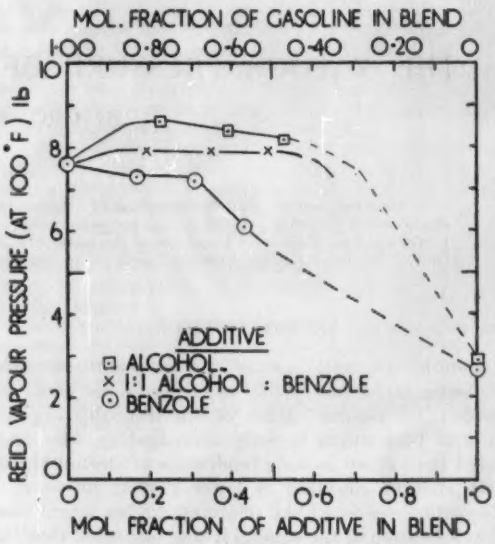

FIG 3

AZEOTROPE FORMATION IN BLENDS

USE OF CHARTS

If the R.V.P. bath is at a temperature other than 100° F, Fig 1 can be used to obtain the correction to be applied to the observed vapour pressure reading to give the gasoline vapour pressure at the bath temperature. This pressure can then be corrected to 100° F or any other desired temperature by means of Fig 2.

AZEOTROPE FORMATION

The exaltation of the vapour pressure of the alcohol–gasoline blends owing to azeotrope formation is clearly shown in Fig 3, where linear relationships should be obtained if the blends obeyed Raoult's law. This azeotropic effect is shown to be significant also for benzole–gasoline blends, but is less than that of the alcohol–gasoline blends. It is obviously very difficult to calculate the vapour pressure of alcohol–benzole–gasoline blends, but, as long as the R.V.P of the final blend meets the required specification, alcohol blends will not show any greater tendency to vapour lock than other gasoline.

ACKNOWLEDGMENT

The author thanks the Management of the South African Torbanite Mining and Refining Co. Ltd for permission to publish this paper.

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[2] Mapstone, G. E. *Refiner*, 1951, **30** (10), 157–9.
[3] Pleeth, S. J. W. *J. Inst. Petrol.*, 1952, **38**, 816.

ALKYLTETRALINS

PART II. THE 2- AND 6-METHYL-, -*n*-PROPYL AND -*n*-BUTYLTETRALINS*

By A. S. BAILEY† and C. M. STAVELEY†

Communicated by J. C. SMITH† (Fellow)

SUMMARY

The 2- and 6-methyl-, -*n*-propyl- and -*n*-butyltetralins have been synthesized by unambiguous methods; the physical properties, including the i.r. and u.v. spectra, have been measured on carefully purified samples. The properties of alkyltetralins obtained in this and in previous investigations are compared.

THE six hydrocarbons here described, along with those of Part I [1] of this series, continue an investigation into the tetrahydro-derivatives of the lower β-*n*-alkylnaphthalenes. With the work of Hipsher and Wise [2] and of Karo, McLaughlin, and Hipsher [3] on the tetrahydro-α-alkylnaphthalenes, and of Mair and Streiff [4] on two methyltetralins, the four homologous series of alkyltetralins may now be compared, at least as to their lower members.

In Figs 1, 2, and 3 the number of carbon atoms in the side-chain is plotted against the boiling point, refractive index, and density respectively of the alkyltetralins. From these curves, two sets of relationships can be observed. (1) It was recorded by Bailey, Pickering, and Smith [5] that the α-alkylnaphthalenes are denser and more refractive than their β- isomers. This behaviour is parallelled by the alkyltetralins; the 1- and 5- substituted compounds are both denser and more refractive than (respectively) their 2- and 6- isomers. (2) Tetralins substituted in the aromatic ring (the 5- and 6- compounds) are denser, more refractive, and higher-boiling than their corresponding isomers substituted in the alicyclic part of the nucleus (the 1- and 2- compounds respectively). This effect may be correlated with the increase in the π electron density caused by the introduction of a third electron-donating substituent into the aromatic nucleus.

Pure samples of alkyltetralins described in the literature have been obtained in various ways—by careful purification of petroleum fractions; [4] by reaction of α-tetralone with the appropriate alkyl Grignard reagent, followed by hydrogenation; [3] by catalytic hydrogenation of 1-alkylnaphthalenes, followed by careful fractional distillation.[2] In some other reported preparations of alkyltetralins less care has been taken to obtain pure end-products, and often widely divergent values are found for the properties of the same compound.

Despite reports in the literature *e.g.*[6] that hydrogenation of β-alkylnaphthalenes gives almost exclusively 6-alkyltetralins, it has been found [7] that the product is a mixture containing not more than two parts of the aromatic substituted (6-) isomer to one part of the alicyclic substituted (2-) compound. However, since the differences in boiling point are less in this series than for the tetrahydro-α-alkylnaphthalenes, syntheses by the route, hydrogenation of β-alkylnaphthalene followed by fractional distillation, is unattractive. The routes adopted, although rather long in the case of the 2- isomers, led to products of unambiguous structure. Recrystallization of the key intermediates, the alkyltetralones and acyltetralins,

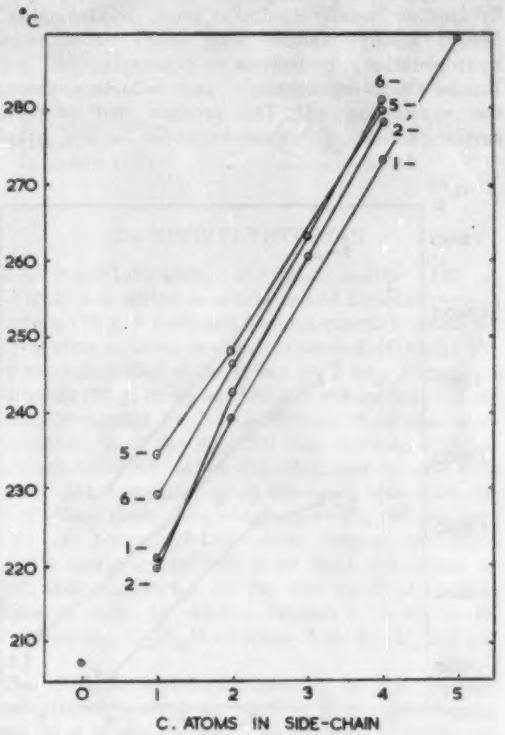


FIG 1

BOILING POINTS (CORRECTED TO 760 MM) OF *n*-ALKYLTETRALINS PLOTTED AGAINST THE NUMBER OF CARBON ATOMS IN THE SIDE-CHAIN

* MS received 17 November 1955.

† The Dyson Perrins Laboratory, Oxford.

ensures a high purity of the final products, although it was not possible to estimate the purity quantitatively.

Of the many routes to 2-alkyltetralins available, the one chosen (treatment of the sodium salt of 2-carbethoxy-1-tetralone with alkyl halide; hydrolysis; and reduction through the semicarbazone of the ketone so obtained) is probably the one to be preferred. When the properties of the sample of 2-methyltetralin obtained in this way were examined, however, they were found to differ quite considerably from the expected values. The boiling point, refractive index, and density were all lower than would have been predicted (for the three other homologous series, smooth curves were obtained on plotting these properties against the number of carbon atoms in the molecule; similar curves could be drawn for the higher 2-alkyltetralins, but these passed considerably above the values actually measured for the methyl homologue). This compound was therefore prepared by another, totally dissimilar route (condensation of benzyl methyl ketone with ethyl cyanoacetate; hydrogenation; hydrolysis to β-benzylbutyric acid; Friedel–Crafts cyclization; and reduction through the semicarbazone). The product had properties agreeing exactly with those found for the first sample.

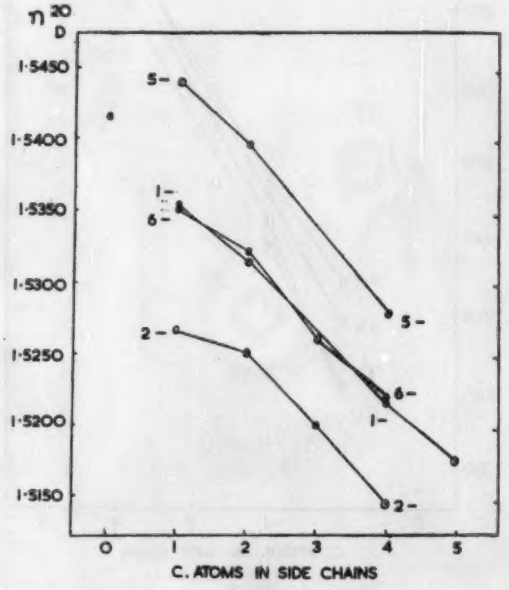


FIG 2

REFRACTIVE INDICES OF n-ALKYLTETRALINS PLOTTED AGAINST THE NUMBER OF CARBON ATOMS IN THE SIDE-CHAIN

The preferred route to 6-alkyltetralins is Friedel–Crafts acylation of tetralin, followed by Huang-Minlon reduction. Since this route is not applicable to the methyl homologue, the latter was prepared from toluene through the well-known succinic anhydride synthesis.

Boiling points of the hydrocarbons were measured under nitrogen with a short-stemmed Anschütz thermometer in a small apparatus incorporating a Cottrell pump; they are correct ±0·2°.

Melting points were measured with an alcohol thermometer immersed in a slowly-melting mush of the hydrocarbon; they are correct ±1·5°. Freezing points could not be measured in the Rossini apparatus owing to the very slow recovery from super-cooling.

Densities were measured in a pycnometer of approx 5 ml capacity.

Refractive indices and *dispersions* ($\mu_f - \mu_c$) were determined on an Abbé instrument, the prisms being maintained at 20° or 25° ± 0·1°.

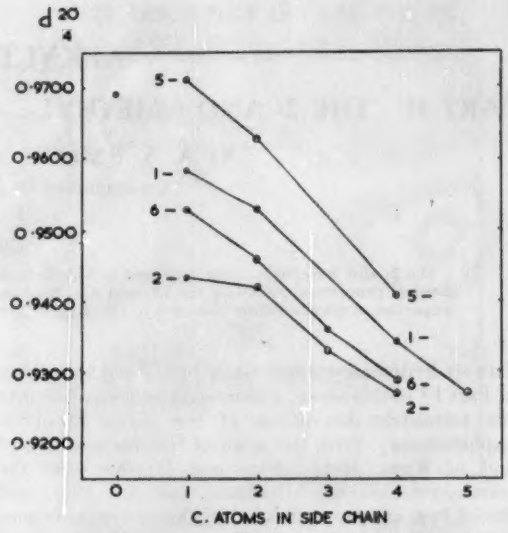
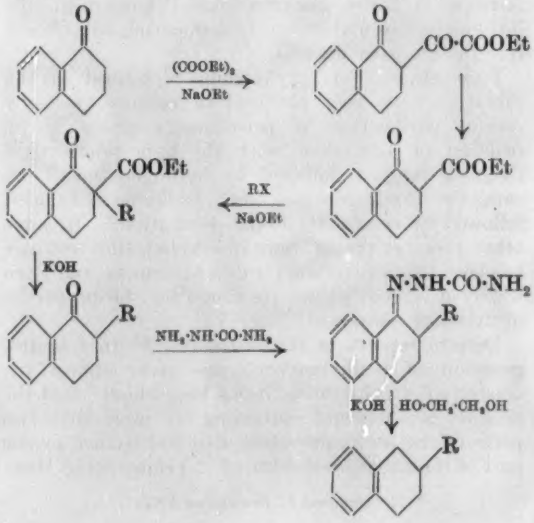


FIG 3

DENSITIES OF n-ALKYLTETRALINS PLOTTED AGAINST THE NUMBER OF CARBON ATOMS IN THE SIDE-CHAIN

EXPERIMENTAL



2-Carbethoxy-1-tetralone. Crude α-tetralone (obtained by peroxidation of tetralin with air [8]) (30 g), diethyl oxalate (60 g), and dry benzene (75 ml) were added in an atmosphere of nitrogen to a suspension of sodium ethoxide [from sodium (9·5 g) in ethanol (120 ml), evaporated to dryness] in dry benzene (200 ml) chilled in ice. The next day, the mixture was poured into ice-water. The aqueous layer was separated, washed with ether, and acidified; the product was extracted with ether, dried, and, after evaporation of the ether, crystallized from ethanol (50 ml) at −10°. There were obtained 22 g (45 per cent yield) of ethyl 1-tetralone-2-glyoxalate of m.p. 47·5°–48°. When pure, recrystallized α-tetralone [1] was used, the yield rose to 87 per cent. (Bachmann and Wendler [9] report a 70 per cent yield of m.p. 44°–45°; Hückel and Goth [10] report m.p. 48°.)

Ethyl 1-tetralone-2-glyoxalate was stirred with half its weight of dry, finely-powdered soda-glass in an oil-bath at 180°–200° for 1–3 hr. The product was distilled from the powdered glass, and then redistilled through a 20-cm Vigreux column. The fraction distilling at 116°–120°/0·2 mm was collected and crystallized from light petroleum at −10°, giving 75–85 per cent yields of 2-carbethoxy-1-tetralone of m.p. 34°–36°. (Hückell and Goth [10] report m.p. 34°.)

2-METHYLTETRALIN

2-Methyl-1-tetralone. 2-Carbethoxy-1-tetralone (100 g, 1 mol) in absolute alcohol (150 ml) was added to a solution of sodium ethoxide (from 11·6 g, 1·1 g atoms of sodium) in absolute alcohol (665 ml). A mixture of methyl iodide (130 g, 2 mol) and ethanol (50 ml) was slowly added, and the solution refluxed for 1 hr. Potassium hydroxide (50 g, 2 mol) in water (100 ml) was then slowly run in, and the solution refluxed for a further 9 hr. Ethanol (400 ml) was distilled from the solution, which was then cooled, cautiously acidified, and diluted with water. The neutral product was then worked up in the usual way; there were obtained 62·7 g (85·5 per cent yield) of liquid of b.p. 126°/12·5 mm.

Twice recrystallized from light petroleum at −15°, this product gave 40 g of pure 2-methyl-1-tetralone of n_D^{20} 1·5541 and m.p. 15·0°. (Found: C, 82·4; H, 7·6. Calc for $C_{11}H_{12}O$: C, 82·5; H, 7·5 per cent.) (English and Cavaglieri [12] report n_D^{21} 1·5585.)

The 2,4-dinitrophenylhydrazone from glycol monoethyl ether formed scarlet needles of m.p. 224°.

The semicarbazone was obtained by mixing 2-methyl-1-tetralone (53 g, 1 mol) in ethanol (400 ml) with semicarbazide hydrochloride (55 g, 1·5 mol) and hydrated sodium acetate (100 g) in water (100 ml), and allowing to stand for two months. The product was washed with water, ethanol, and petroleum; a sample, recrystallized from ethanol, had m.p. 196°–197°. (Found: C, 66·3; H, 7·1; N, 19·0. Calc for $C_{12}H_{15}ON_3$: C, 66·4; H, 6·9; N, 19·3 per cent). (Titley [11] reports m.p. 200°–201°, English and Cavaglieri [12] report 199°.)

2-Methyltetralin. 2-Methyl-1-tetralone semicarbazone (from 53 g of ketone) was heated ½ hr under reflux in a solution of potassium hydroxide (61 g) in ethylene glycol (450 ml). With the condenser set for distillation the liquid was boiled until its temperature reached 194° and the distillate was collected. Refluxing was then resumed for 4 hr.

The solution was cooled, diluted with water, the distillate up to 194° added, and the mixture extracted with ether. The extract was washed with water, and after drying and evaporating there were obtained 36·7 g (76 per cent yield, based on ketone) of distilled product. Fractionally distilled through a Bower and Cooke [13] column (a reflux ratio of 18 : 1 being used), the crude preparation yielded a small fraction, b.p. 108°–110·5°/27 mm and n_D^{20} 1·5262–1·5266, and then five fractions, all of b.p. 110·5°/27 mm and n_D^{20} 1·5267, weighing 25·6 g. These fractions were combined, stirred with sodium metal at 160°, and distilled. The pure final product (found: C, 90·4; H, 9·8. Calc for $C_{11}H_{14}$: C, 90·4; H, 9·6 per cent) had the following constants:

Boiling point	219·8°/751 mm
Melting point	−43·1°
Refractive Index	n_D^{20} 1·5267; n_D^{25} 1·5243
Density	d_4^{20} 0·9432
Dispersion (20°)	$\mu_f - \mu_r = 0·0149$

2-*n*-PROPYLTETRALIN

2-n-Propyl-1-tetralone. *n*-Propyl iodide (102 g, 1·75 mol) was added to a solution of 2-carbethoxy-1-tetralone (75 g, 1 mol) and sodium ethoxide (from 8·7 g, 1·1 g atom sodium) in absolute alcohol (500 ml); the mixture was boiled under reflux for 2 hr. Potassium hydroxide (80 g) in water (100 ml) was added, and refluxing continued for 5 hr. 400 ml of alcohol were evaporated, and the solution was cooled, acidified (with evolution of carbon dioxide), and diluted with water. After working up in the usual way with the aid of ether, there were obtained 55·8 g (86 per cent yield) of 2-*n*-propyl-1-tetralone boiling at 148°–156°/12 mm; crystallized from light petroleum at −10°, this gave 44·8 g (69 per cent yield) of purified ketone of m.p. 43°–43·5°. (Found: C, 82·7; H, 8·6 per cent. $C_{13}H_{16}O$ requires C, 83·0; H, 8·5 per cent.)

The 2,4-dinitrophenylhydrazone, orange needles from ethanol, melted at 146·5°. The *semicarbazone* (from 54 g of the ketone; the reaction mixture was allowed to stand for 3 months before working up) had m.p. 185°; a small sample, crystallized from ethanol, formed small rods of m.p. 185·5°. (Found: C, 69·0; H, 7·9; N, 16·8. $C_{14}H_{19}ON_3$ requires C, 68·6; H, 7·7; N, 17·1 per cent.)

2-n-Propyltetralin. The semicarbazone of 2-*n*-propyl-1-tetralone (from 54 g ketone) was converted to the hydrocarbon in the manner described above for 2-methyltetralin. The crude, distilled product, weighing 34 g (68 per cent yield), was fractionally distilled through the Bower and Cooke [13] column

(reflux ratio, 20 : 1) at a pressure of 18 mm. After small initial fractions of b.p. 75°–112·4° and n_D^{20} 1·5090–1·5204, there were obtained four fractions, all of b.p. 112·4° and n_D^{20} 1·5202, weighing 22·9 g. These were combined, stirred with sodium metal at 160° for ½ hr, and redistilled. The product (found: C, 89·7; H, 10·6. $C_{12}H_{18}$ requires C, 89·6; H, 10·4 per cent) had the following constants:

Boiling point	260·1°/750 mm
Melting point	−7·5°
Refractive Index	n_D^{20} 1·5202; n_D^{25} 1·5182
Density	d_4^{20} 0·9331
Dispersion (20°)	$\mu_f - \mu_c = 0·0140$

2-*n*-BUTYLTETRALIN

2-n-*Butyl*-1-*tetralone*. *n*-Butyl bromide (125 g) was added to a solution of 2-carbethoxy-1-tetralone (105·5 g) and sodium ethoxide (from 11·6 g of sodium) in absolute alcohol (800 ml). The solution was refluxed for 7 hr; potassium hydroxide (100 g) in water (100 ml) was added, and refluxing continued for 7 hr. After the evaporation of 400 ml of ethanol, the solution was cooled, acidified, and diluted with water. The neutral product, worked up with the aid of ether, weighed 82 g and had b.p. 30°–165°/12 mm. Redistilled through a 20-cm Vigreux column, this gave a main fraction, weighing 67·8 g, of b.p. 145°–160°/12 mm, which was crystallized successively from light petroleum and acetone at −78° to give 41 g of pure 2-*n*-butyl-1-tetralone of b.p. 164°/15 mm, n_D^{20} 1·5358, and m.p. 11·4°–11·8°. (Found: C, 83·1; H, 8·8. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9 per cent.)

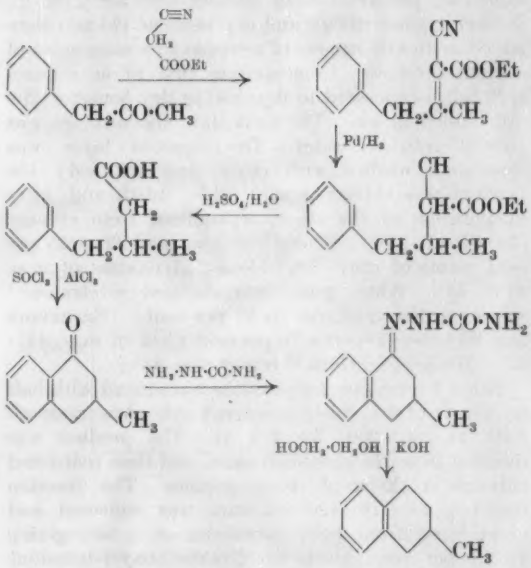
The 2, 4 - *dinitrophenylhydrazone* crystallized from ethanol in orange platelets of m.p. 144°. (Found: N, 14·5. $C_{20}H_{22}O_4N_4$ requires N, 14·7 per cent.)

The *semicarbazone* (from 41 g of the ketone; the reaction mixture was allowed to stand 3½ months before being worked up) was not purified *in toto*; a sample, crystallized from glycol monoethyl ether, melted at 150·5°. (Found: C, 69·5; H, 8·4 per cent. $C_{15}H_{21}ON_3$ requires C, 69·5; H, 8·1 per cent.)

2-n-*Butyltetralin*. The semicarbazone from 41 g of 2-*n*-butyl-1-tetralone was converted to the hydrocarbon in the manner described above for 2-methyltetralin. The crude, distilled product, weighing 30·5 g (80 per cent yield), was fractionally distilled through the Bower and Cooke [13] column (reflux ratio 20 : 1) at a pressure of 8 mm. After small initial fractions of b.p. 116°–125·5° and n_D^{20} 1·5180–1·5160, four fractions, all of b.p. 125·5° and n_D^{20} 1·5160 and weighing 21·9 g, were collected. These last were mixed, stirred with sodium metal at 160° for ½ hr, and redistilled. The product (found: C, 89·2; H, 10·8. $C_{14}H_{20}$ requires C, 89·4; H, 10·6 per cent) had the following constants:

Boiling point	278·8°/763 mm
Melting point	−30·1°
Refractive Index	n_D^{20} 1·5161; n_D^{25} 1·5141
Density	d_4^{20} 0·9273
Dispersion (20°)	$\mu_f - \mu_c = 0·0134$

2-METHYLTETRALIN (Second Route)



Ethyl 2-Cyano-3-benzylcrotonate. Benzyl methyl ketone (100 g, 1 mol), ethyl cyanoacetate (84·9 g, 1 mol), ammonium acetate (11·7 g, 0·2 mol), acetic acid (36 g, 0·8 mol), and benzene (150 ml) were boiled under a constant water separator for 8 hr. The cooled solution was washed with water and with sodium hydroxide solution, and, after evaporation of the benzene, left a residue boiling at 136°–160°/1 mm. On cooling, the distillate partly crystallized; it was mixed with a light petroleum–benzene mixture (300 ml of 1 : 1), allowed to stand 3 hr, and filtered. After working up the filtrate, there were obtained 98 g (57 per cent yield) of the ester of b.p. 120°–130°/0·4 mm and n_D^{20} 1·5338. Cope *et al* [14] report n_D^{25} 1·5338; Hugh and Kon [15] report n_D^{19} 1·53401.

Ethyl 2-Cyano-3-benzylbutyrate. Portions of ethyl 2-cyano-3-benzylcrotonate in twice their volume of ethanol were shaken with 1·5 per cent palladized strontium carbonate under hydrogen at 5 atm pressure. The theoretical volume (1 mol) of hydrogen was absorbed. After working up, the product had b.p. 121°–123°/0·5 mm and n_D^{20} 1·4997–1·4999.

β-*Benzylbutyric Acid*. Ethyl 2-cyano-3-benzylbutyrate (124 g), acetic acid (250 ml), *conc* sulphuric acid (125 ml), and water (125 ml) were boiled under reflux for 10 hr. The acidic product was then worked up in the usual way; it had b.p. 120°–130°/0·5 mm, n_D^{20} 1·5120, and weight 60·5 g (63 per cent yield). (Tucker *et al* [16] report b.p. 275°–277°.)

The *amide* crystallized from light petroleum as a powder of m.p. 80·5°. (Found: C, 74·5; H, 8·41. $C_{11}H_{15}ON$ requires C, 74·6; H, 8·47 per cent.)

The *anilide* crystallized from 50 per cent aqueous ethanol in needles of m.p. 103·5°. (Found: C, 80·5; H, 7·43; N, 5·2. $C_{17}H_{19}ON$ requires C, 80·7; H, 7·51; N, 5·5 per cent.)

3-*Methyl*-1-*tetralone*. β-Benzylbutyryl chloride, obtained by the action of thionyl chloride (55 g, 1·4 mol) on β-benzylbutyric acid (60·5 g, 1 mol), in carbon disulphide (165 ml) was chilled in ice, and treated with powdered aluminium chloride (50 g, 1·1 mol) added in small portions. The mixture was boiled under reflux for 1½ hr, chilled, and decomposed with ice and *conc* hydrochloric acid. The neutral product was worked up in the usual way, and on distillation gave a main fraction of b.p. 136°–138°/15 mm, n_D^{20} 1·5520, m.p. 16·5°, and weight 41·5 g (74·5 per cent yield). Recrystallization from light petroleum gave a product of m.p. 16·9° and n_D^{20} 1·5522, unchanged by further crystallization. (Found: C, 83·0; H, 7·47. Calc for $C_{11}H_{12}O$: C, 82·5; H, 7·50 per cent.)

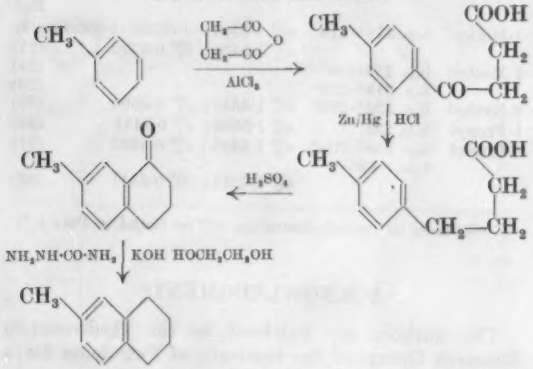
The 2,4-dinitrophenylhydrazone crystallized from glycol monoethyl ether as an orange powder of m.p. 241°.

The semicarbazone, crystallized from aqueous ethanol, had m.p. 189°. (Found: C, 66·4; H, 6·9. Calc for $C_{12}H_{15}ON_3$: C, 66·4; H, 6·9 per cent.) (Buu-Hoï and Cagniant [17] report m.p. 177°, Tucker *et al* [16] report 179°–188°, Jones and Ramage [18] 189°, Tishler *et al* [19] report 195°–196°; *DNP*, m.p. 242°.[16, 20])

2-*Methyltetralin*. 3-Methyl-1-tetralone semicarbazone (from 47 g of ketone) was converted to the hydrocarbon in the manner described for 2-methyl-1-tetralone. A residue, obtained after distillation of the crude hydrocarbon, crystallized from light petroleum in orange prisms of m.p. 128·5°. (Found: C, 83·2; H, 7·7. The *azine*, $C_{22}H_{24}N_2$, requires C, 83·5; H, 7·6 per cent.) The hydrocarbon (38·5 g) was fractionally distilled through the Bower and Cooke [13] column with a reflux ratio of 22 : 1. After small low-boiling fractions, there were obtained four fractions, all of b.p. 121·5°/46 mm and n_D^{20} 1·5267, weighing 24·3 g. They were mixed, stirred with sodium at 160° for ½ hr, and redistilled. The product (found: C, 90·5; H, 9·9. Calc for $C_{11}H_{14}$: C, 90·4; H, 9·6 per cent) had the following properties:

Boiling point	220·0°/757 mm (1st Prep.)	219·8°/751 mm
Melting point	−43·4°	−43·1°
Refractive Index	n_D^{20} 1·5267	n_D^{20} 1·5267
Density	d_4^{20} 0·9432	d_4^{20} 0·9432

6-METHYLTETRALIN



(Following Barnett and Sanders.[21])

β-*p*-Toluylpropionic acid of m.p. 127·5° was obtained from toluene, succinic anhydride, and aluminium chloride in 81 per cent yield after recrystallization from benzene. (Bailey *et al* [22] report m.p. 129°.)

Clemmensen reduction of this gave γ-*p*-tolylbutyric acid in 84 per cent yield; after recrystallization from light petroleum it had m.p. 59°. (Barnett and Sanders [21] report m.p. 59°.)

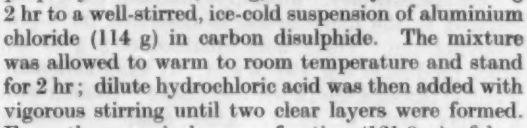
The acid was cyclized with 80 per cent sulphuric acid. 7-Methyl-1-tetralone was obtained in 73 per cent yield, and after crystallization from light petroleum had m.p. 34°. (Barnett and Sanders [21] report m.p. 35°, Bailey *et al* [22] report 33·5°.)

The ketone (48 g) was converted to the semicarbazone; a sample, crystallized from ethanol: glycol monoethyl ether (1 : 1) had m.p. 228°. (Found: C, 66·4; H, 6·8; N, 19·5. Calc for $C_{12}H_{15}ON_3$: C, 66·4; H, 6·8; N, 19·35 per cent.) (Sah [23] reports m.p. 232°.)

The semicarbazone was converted to the hydrocarbon as described for 2-methyltetralin. After distillation of the crude hydrocarbon a residue was obtained which, crystallized from light petroleum, formed a mat of pale yellow needles of m.p. 146°. (Found: C, 82·9; H, 7·4; N, 8·8. The *azine*, $C_{22}H_{24}N_2$, requires C, 83·5; H, 7·6; N, 8·9 per cent.) The hydrocarbon was fractionally distilled through the Bower and Cooke [13] column with a reflux ratio of 20 : 1. After some initial low-boiling fractions, three fractions, all with b.p. 124·1°/37 mm and n_D^{20} 1·5352, and weighing 20 g, were collected. These were mixed, stirred with sodium at 160° for ½ hr, and redistilled. The product (found: C, 90·3; H, 9·5. Calc for $C_{11}H_{14}$: C, 90·4; H, 9·6 per cent) had the following properties:

Boiling point	229·1°/758 mm
Melting point	−38·7°
Refractive Index	n_D^{20} 1·5352; n_D^{25} 1·5330
Density	d_4^{20} 0·9529
Dispersion (20°)	$\mu_F - \mu_C = 0·0156$

6-*n*-PROPYLTETRALIN



6-*Propionyltetralin*. A mixture of purified tetralin (99 g of m.p. −36·2°, n_D^{20} 1·5417) and freshly prepared propionyl chloride (92·2 g) was slowly added during 2 hr to a well-stirred, ice-cold suspension of aluminium chloride (114 g) in carbon disulphide. The mixture was allowed to warm to room temperature and stand for 2 hr; dilute hydrochloric acid was then added with vigorous stirring until two clear layers were formed. From the organic layer, a fraction (121·8 g) of b.p.

130°–140°/0·9 mm and m.p. −8° to −5° was obtained. This was twice recrystallized from a 10 per cent solution in light petroleum at −78°; the purified product, weighing 63 g, had b.p. 166°–170°/14 mm, m.p. −2·5° to −1·6°, and n_D^{20} 1·5537.

The semicarbazone crystallized from ethanol in small needles of m.p. 200°. (Found: N, 17·1. Calc for $C_{14}H_{19}ON_3$: N, 17·1 per cent.) The *2,4-dinitrophenylhydrazone*, a brick-red powder from ethanol had m.p. 199°.

Smith and Lo [24] report n_D^{20} 1·5508, semicarbazone m.p. 209°; Barbot [25] reports n_D^{23} 1·550, semicarbazone m.p. 224°–225°.

6-n-*Propyltetralin*. 6-Propionyltetralin (63 g) was added to a solution of potassium hydroxide (71·5 g) and hydrazine hydrate (52 ml of 90 per cent) in diethylene glycol (520 ml). The mixture was boiled under reflux for 45 min; the condenser was set for distillation, and the liquid boiled (the distillate being collected) until its temperature reached 197°, when refluxing was resumed for 4 hr. The cooled mixture was diluted with water, and the hydrocarbon, extracted from it with the aid of ether, was distilled; it weighed 48·7 g (83 per cent yield).

The crude hydrocarbon was fractionally distilled through the Bower and Cooke [13] column with a reflux ratio of 16 : 1. After three low-boiling fractions had been collected, the bulk of the material (26 g) distilled in four fractions, all of b.p. 117·1°/9 mm and n_D^{20} 1·5263. These were mixed, stirred with sodium at 160° for ½ hr, and redistilled. The product (found: C, 89·4; H, 10·3. Calc for $C_{13}H_{18}$: C, 89·6; H, 10·4 per cent) had the following properties:

Boiling point	262·1°/748 mm
Melting point	−51·7°
Refractive Index	n_D^{20} 1·5263; n_D^{25} 1·5242
Density	d_4^{20} 0·9359
Dispersion (20°)	$\mu_f - \mu_c$ = 0·0146

6-*n*-BUTYLTETRALIN

6-n-*Butyryltetralin*. Tetralin (112 g) and *n*-butyryl chloride (112 g) were added to aluminium chloride (125 g) in carbon disulphide (720 ml) chilled in ice. The crude product had b.p. 170°–174°/13 mm, m.p. −4°, n_D^{20} 1·5464, and weight 160 g (93 per cent yield). Two recrystallizations from a 20 per cent solution in acetone at −78° gave a product of b.p. 125°/1 mm, m.p. 6·5°, and n_D^{20} 1·5468. (Barbot [25] reports n_D^{25} 1·5460.)

The 2,4-*dinitrophenylhydrazone* crystallized from glycol monoethyl ether in red needles of m.p. 201°. (Found: N, 14·7. $C_{20}H_{22}O_4N_4$ requires: N, 14·7 per cent.)

6-n-*Butyltetralin*. 6-*n*-Butyryltetralin (80 g) was reduced to the hydrocarbon as described for 6-propionyltetralin. There were obtained 63·2 g of the crude product of b.p. 130°/8 mm. It was fractionally distilled through the Bower and Cooke [13] column with a reflux ratio of 16 : 1. After small low-boiling fractions, there were collected six fractions with a total weight of 43·3 g, all of b.p. 129·9°/8 mm and n_D^{20} 1·5220. These were mixed, stirred with sodium at 160° for ½ hr, and redistilled. The product (found: C, 89·2; H, 10·3. $C_{14}H_{20}$ requires: C, 89·4; H, 10·6 per cent) had the following properties:

Boiling point	281·2°/764 mm
Melting point	Failed to crystallize even at −78°
Refractive Index	n_D^{20} 1·5220; n_D^{25} 1·5200
Density	d_4^{20} 0·9286
Dispersion (20°)	$\mu_f - \mu_c$ = 0·0142

Table I is not exhaustive, but contains only the best recorded values for each compound. Boiling points obtained in the present investigation are corrected to a pressure of 760 mm by assuming dt/dp = 0·04°/mm. Sources: *a*, from petroleum; *b*, tetralone synthesis; *c*, by hydrogenation of an alkylnaphthalene, followed by fractional distillation.

TABLE I

The Best Properties of Alkyltetralins Drawn from The Literature

Substituents	B.p./760 mm	F.p.–m.p.	n_D^{20}	d_4^{20}	Source	Ref.
Nil	207·41°	−35·82°	1·5415	0·96935	*a*	(3)
Nil	207·57°	−35·80°	—	—	*a*	(4)
1-Methyl-	220·54°	—	1·5353	0·95825	*b*	(3)
1-Methyl-	220·46°	—	1·5354	0·95850	*c*	(2)
2-Methyl-	220·2°	−43·1°	1·5267	0·9432	Present work	
5-Methyl-	234·20°	−23·05°	1·5440	0·97106	*c*	(3)
5-Methyl-	234·35°	−22·90°	1·5439	0·9720	*a*	(4)
6-Methyl-	229·03°	−39·75°	1·5357	0·9537	*a*	(4)
6-Methyl-	229·2°	−38·7°	1·5352	0·9529	Present work	
1-Ethyl-	239·46°	—	1·5318	0·95285	*b*	(3)
1-Ethyl-	239·40°	—	1·5316	0·95230	*c*	(2)
1-Ethyl-	239·4°	—	1·5319	0·9542	Part I [1]	(1)
2-Ethyl-	242·6°	−48·38° −42·75°	1·5252	0·9420	Part I [1]	(1)
5-Ethyl-	248·02°	−44·55°	1·5398	0·96286	*c*	(2)
5-Ethyl-	248·0°	−44·70°	1·5399	0·9628	Part I [1]	(1)
6-Ethyl-	246·5°	—	1·5322	0·9460	Part I [1]	(1)
2-*n*-Propyl-	260·5°	— 7·5°	1·5202	0·9331	Present work	
6-*n*-Propyl-	262·6°	−51·7°	1·5263	0·9359	Present work	
1-*n*-Butyl-	273·00°	—	1·5218	0·93418	*b*	(3)
1-*n*-Butyl-	273·06°	—	1·5220	0·93501	*c*	(2)
2-*n*-Butyl-	278·7°	−30·1°	1·5161	0·9273	Present work	
5-*n*-Butyl-	279·91°	−49°	1·5280	0·94093	*c*	(2)
6-*n*-Butyl-	281·0°	—	1·5220	0·9286	Present work	
1-*n*-Pentyl-	289·49°	—	1·5178	0·92705	*b*	(3)

TABLE II

Other Preparations of n-*Alkyltetralins in The Literature*

			Ref.
1-Methyl	b.p. 218°–219°	n_{He}^{25} 1·53316–1·53332–1·53366	(26)
		n_D^{20} 1·5451; d_4^{20} 0·9726	(27)
2-Methyl	b.p. 228–230°		(28)
	b.p. 218°–220°		(29)
6-Methyl	b.p. 224°–226°	n_D^{20} 1·5352; d_4^{20} 0·9504	(30)
1-Propyl	b.p. 253°	n_D^{25} 1·5250; d_4^{25} 0·9415	(26)
6-Propyl	b.p. 256°–258°	n_D^{20} 1·5308; d_4^{20} 0·9395	(31)
	f.p. −68°		
		n_D^{20} 1·5234; d_4^{20} 0·9341	(32)

(References to the ethyltetralins will be found in Part I.[1])

ACKNOWLEDGMENTS

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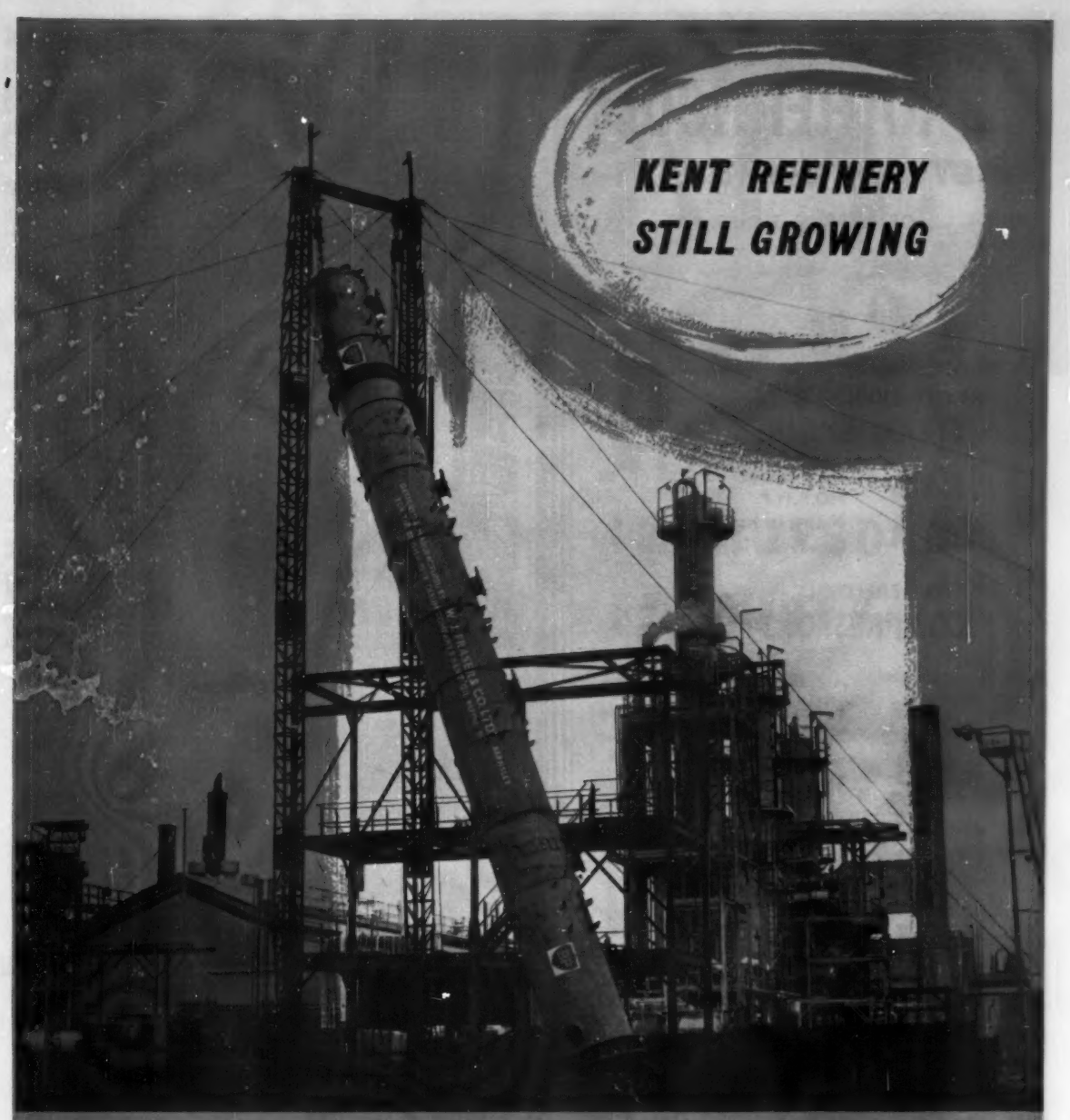

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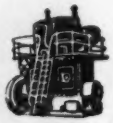

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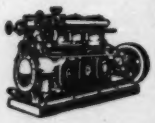

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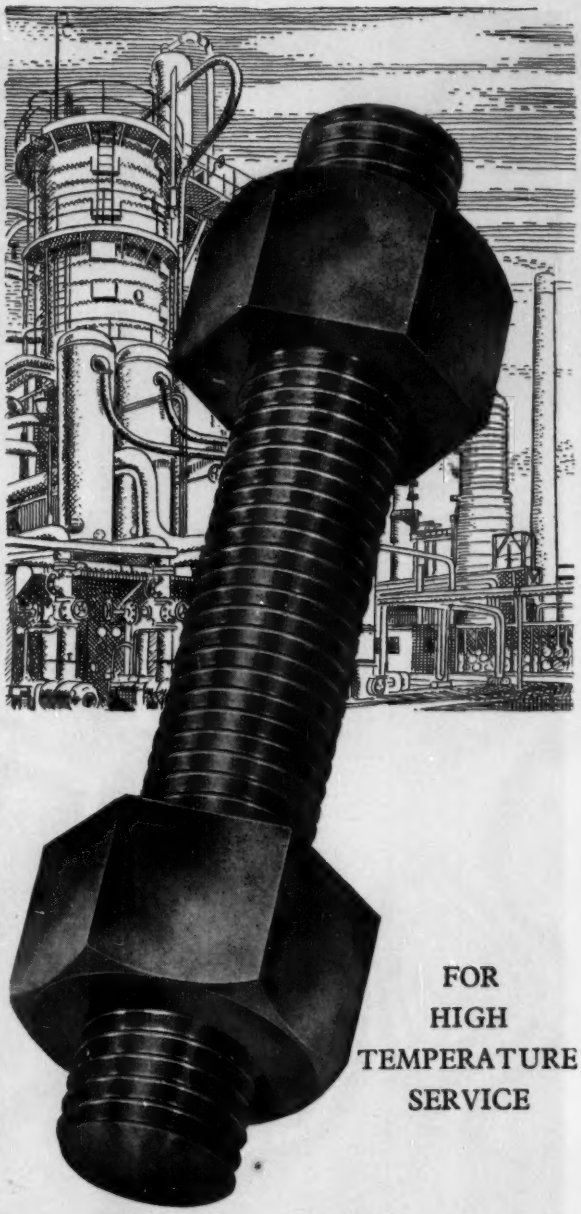

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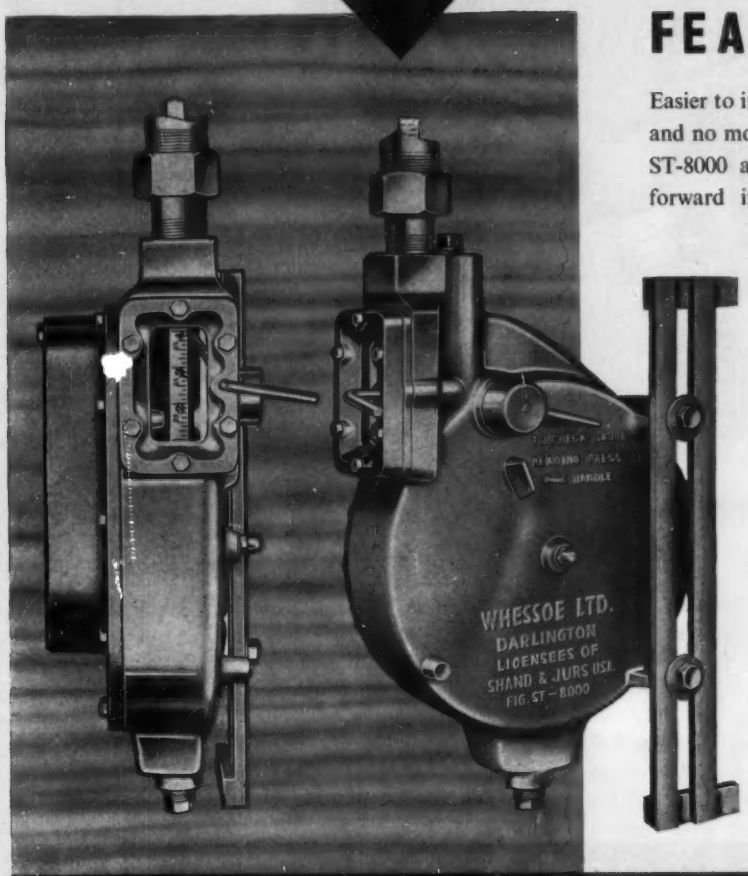

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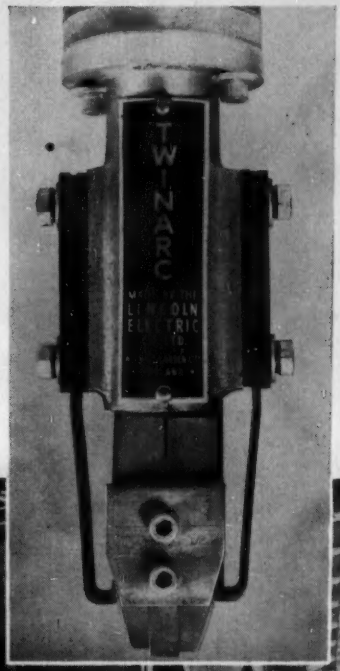

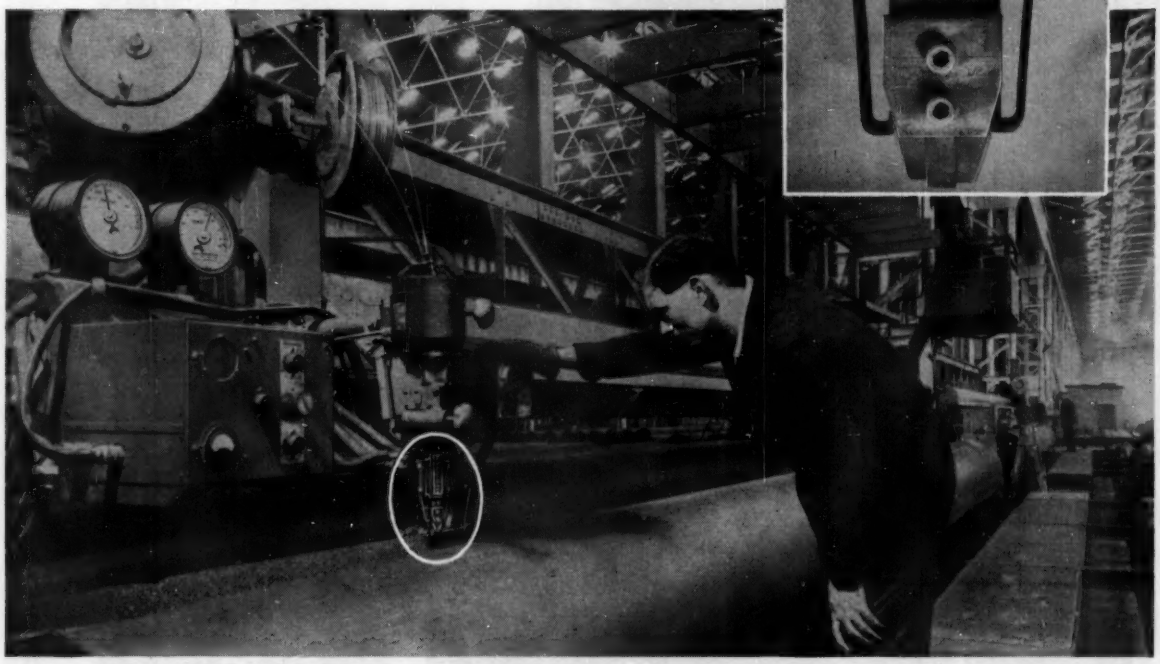

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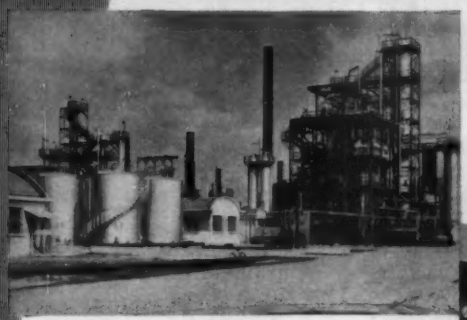
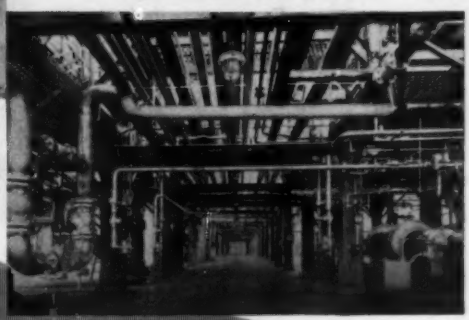


General view of crude, visbreaking, desulphurising, recovery and stabilisation units.

Graphic type panels are installed on both sides of control room with operator desk panels in centre. Crude and visbreaker unit panel is illustrated.

General view of Refinery with Mantova in background.



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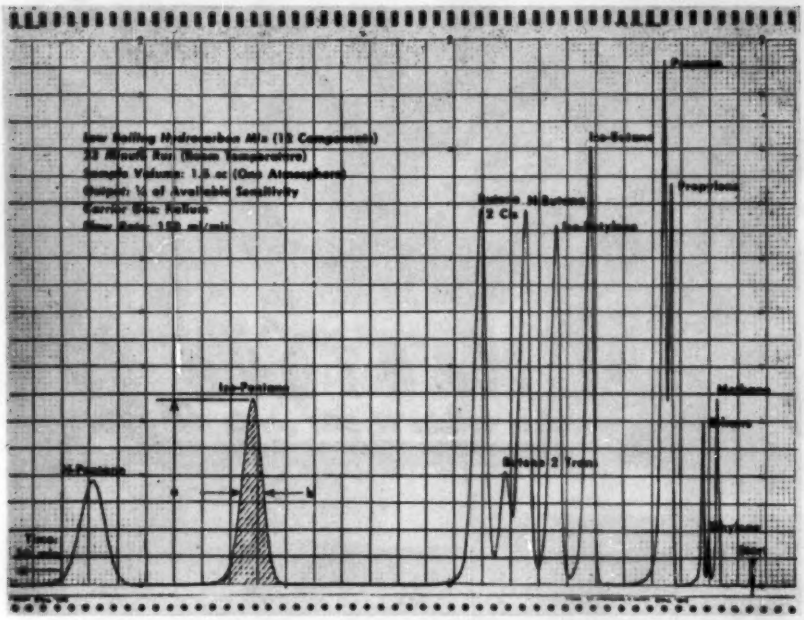

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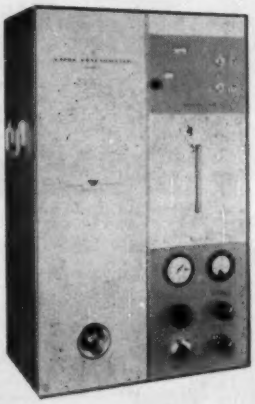

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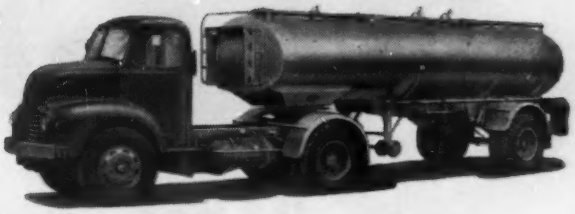

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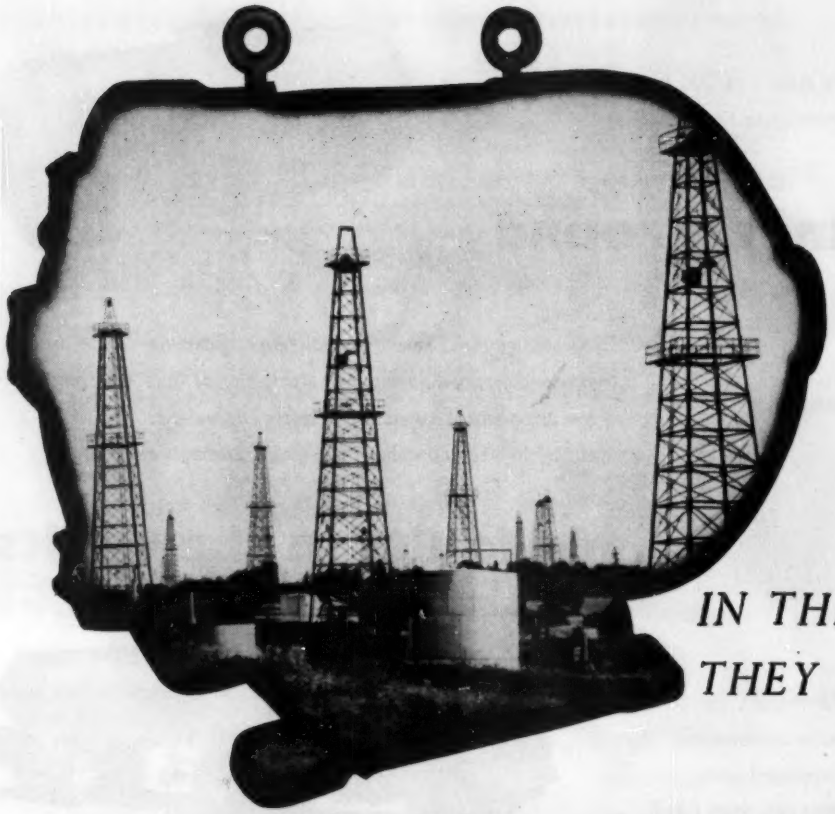

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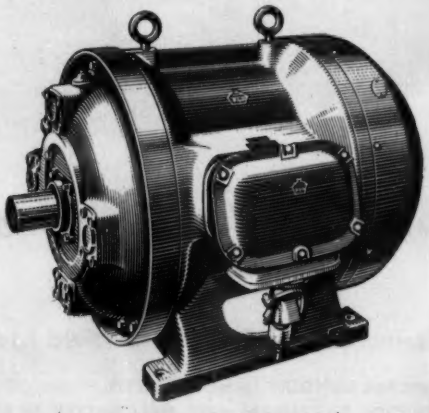

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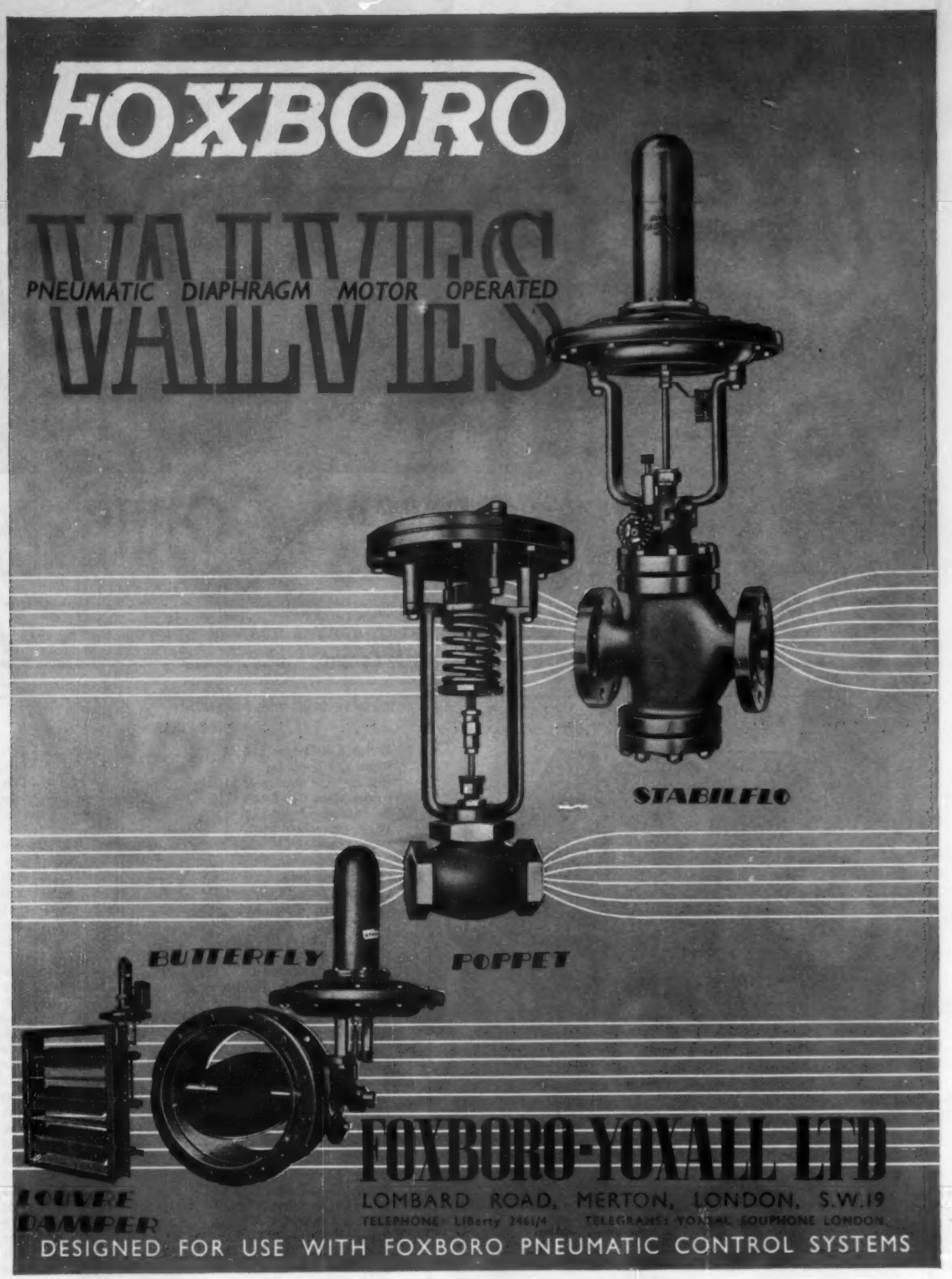
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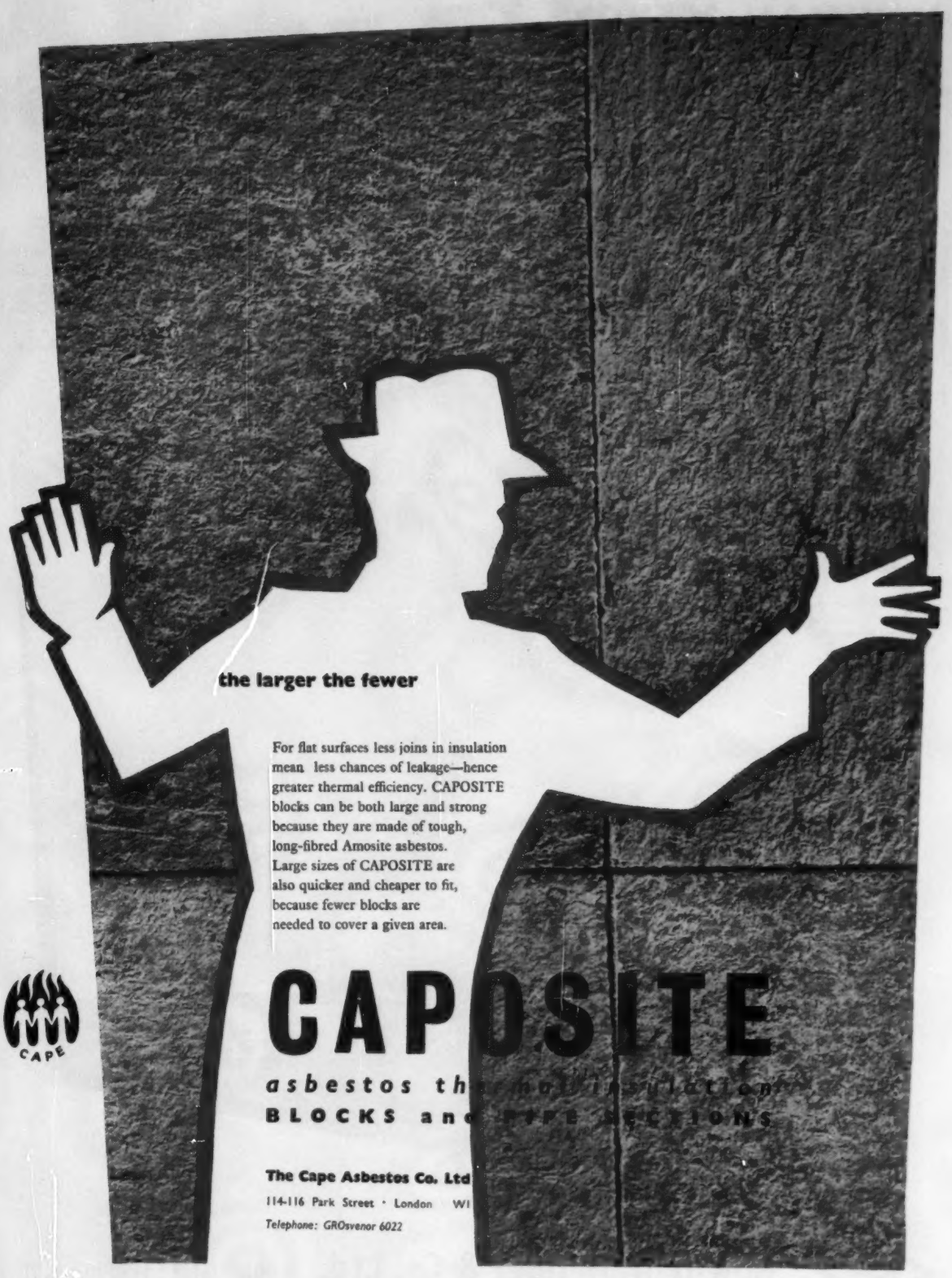

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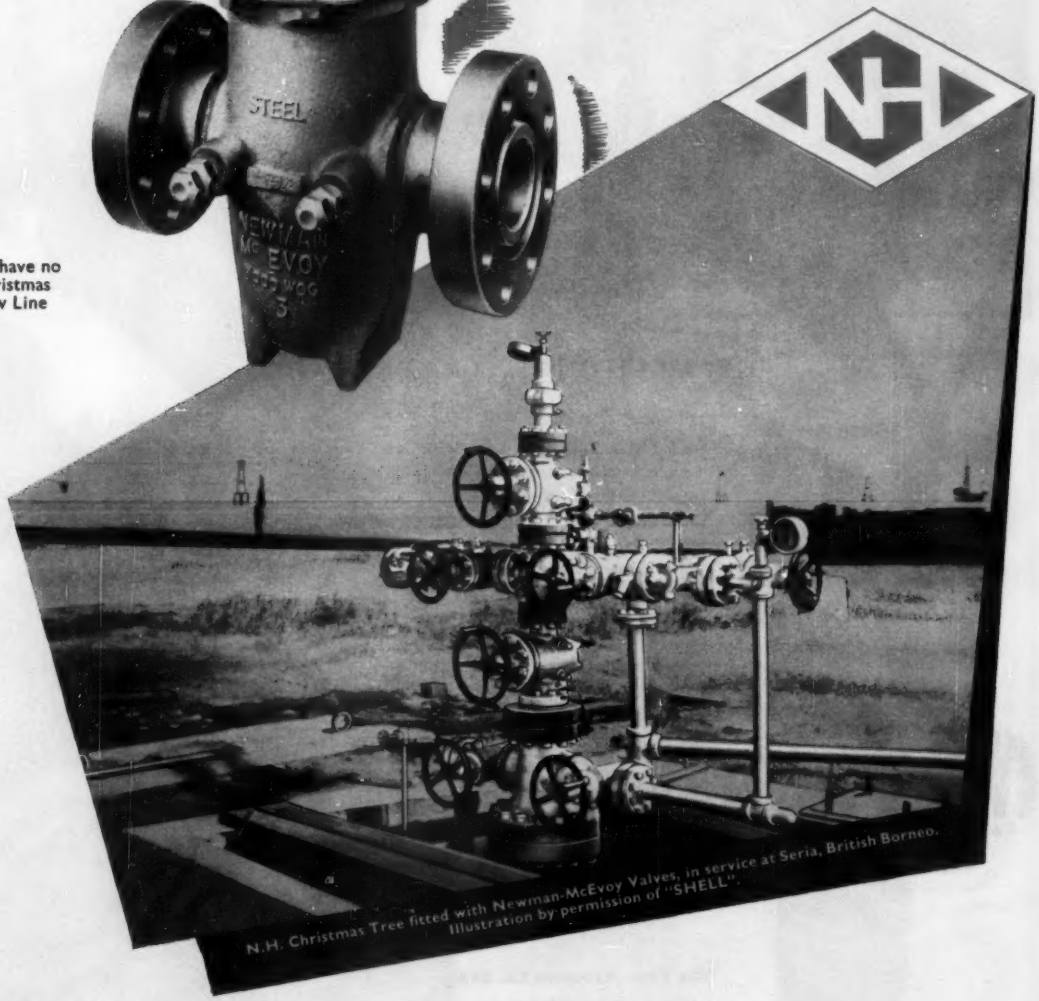

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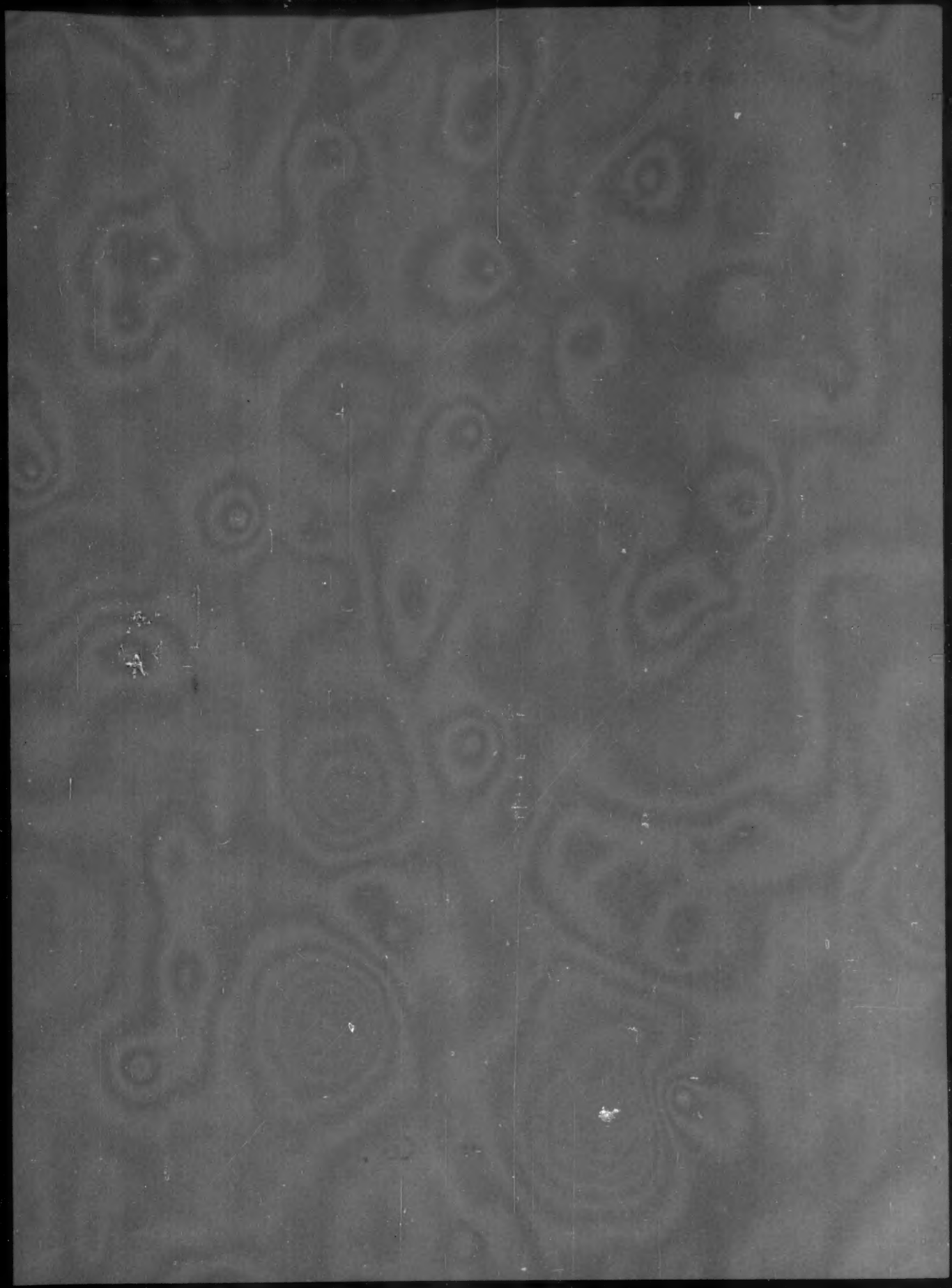

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